THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

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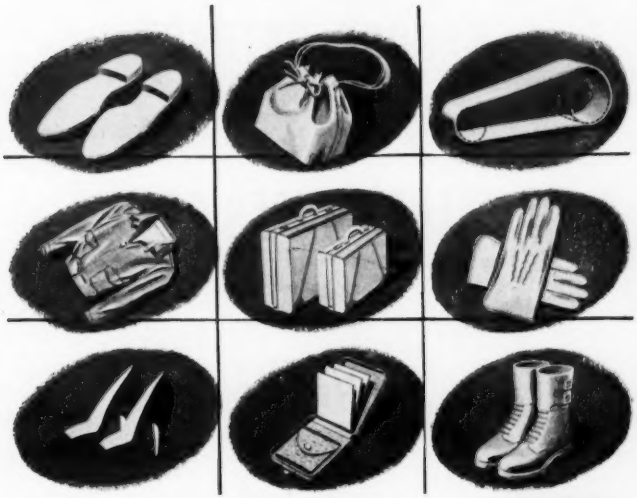

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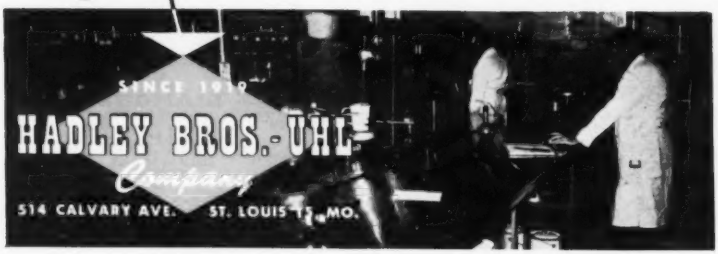

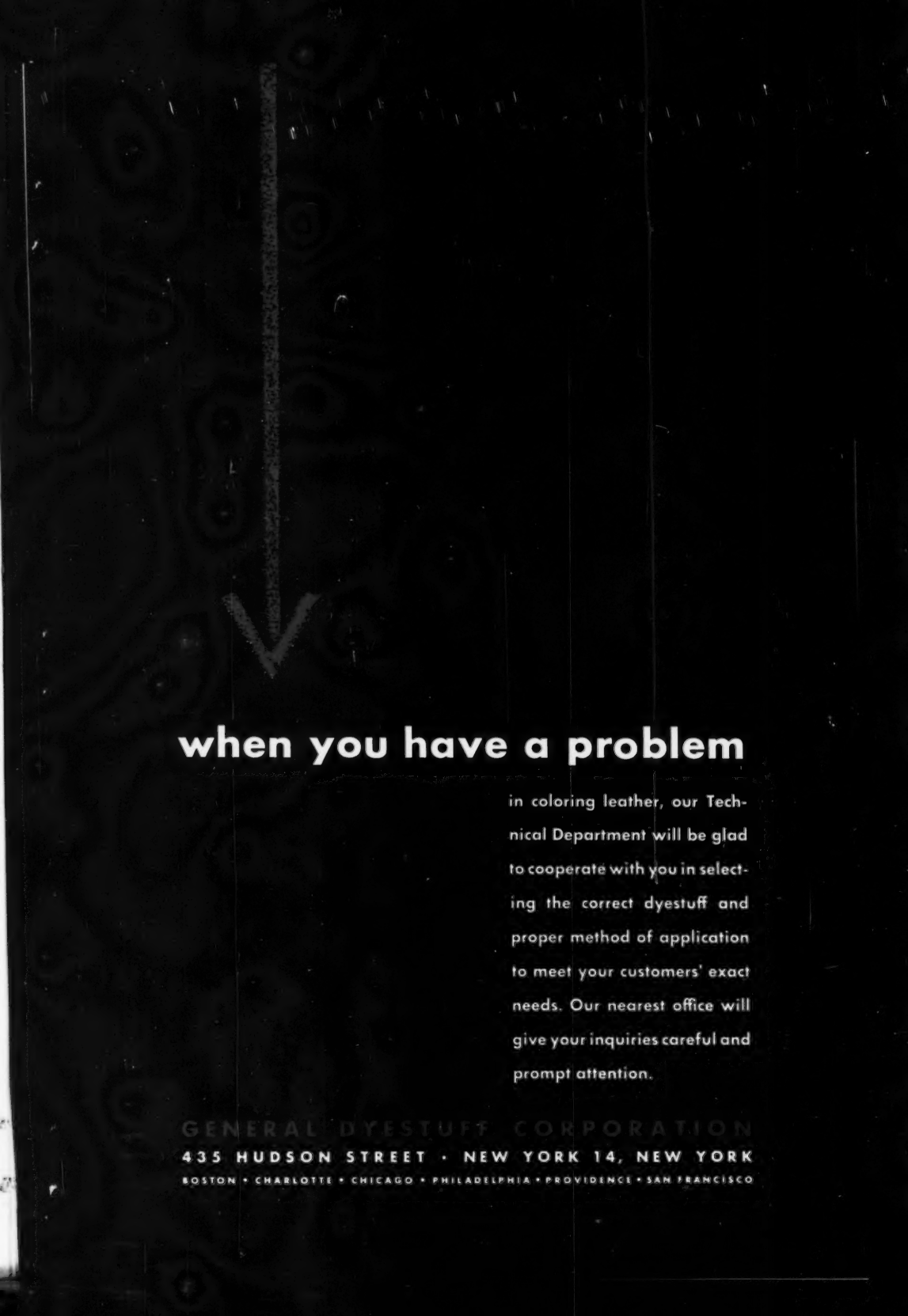
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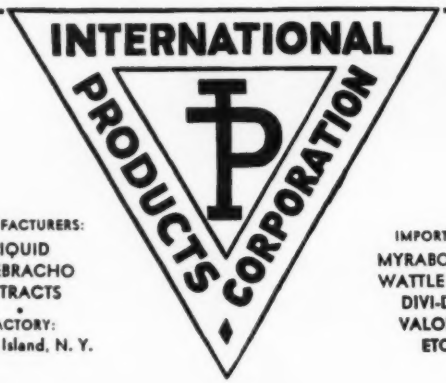

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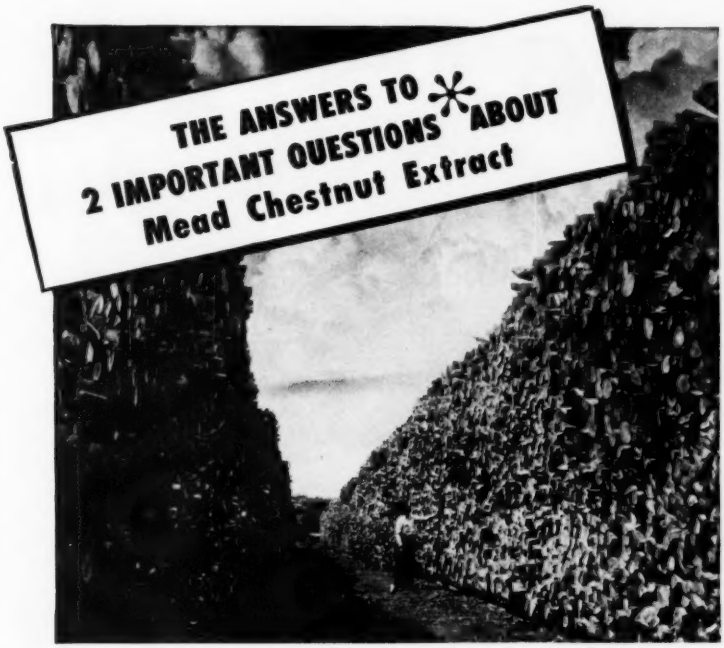

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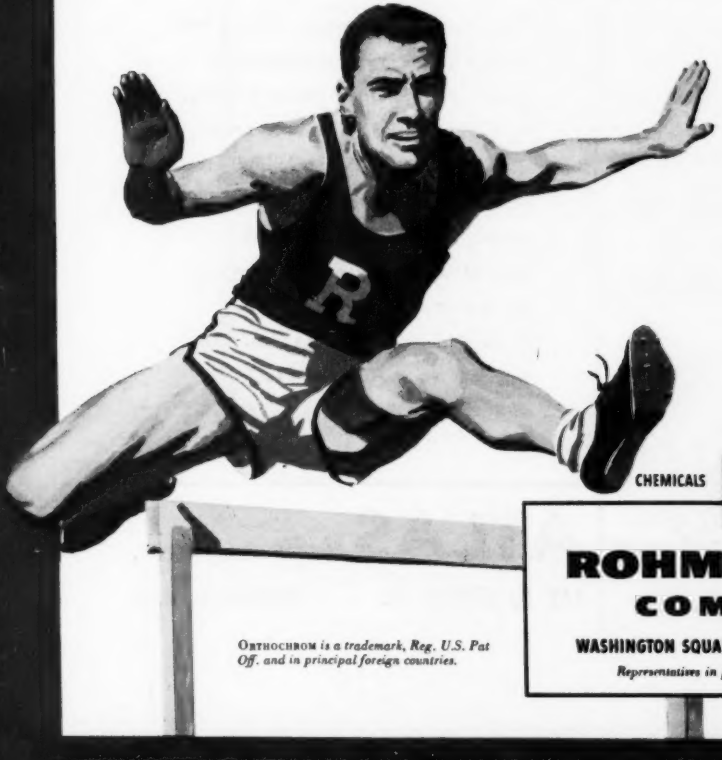

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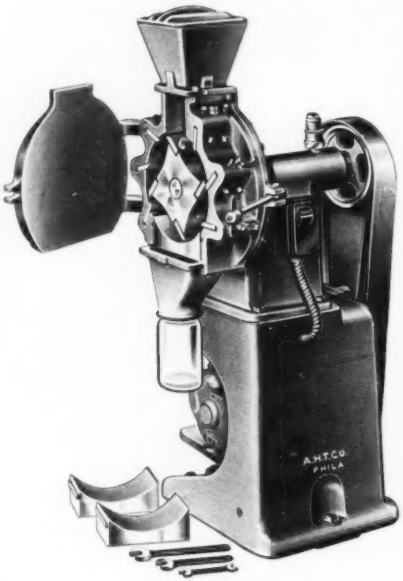

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G. H. Jennings, American Oak Chrome Retan Division, Howes Leather Company, Inc., Dalton & Flint Sts., Cincinnati 14, Ohio.
Philip J. Kraft, Jr., 61–63 Oliver Street, Boston, Massachusetts.
Charles W. Lizer, W. D. Byron & Sons of Maryland, Williamsport, Maryland.
Alfred McIlvaine, 243 Jackson Street, Bristol, Pennsylvania.
Stuart E. Miller, Jr., c/o S. H. Frank & Company, P. O. Box 471, Redwood City, California.
Paul H. Mugford, 27 Waldron Street, Marblehead, Massachusetts.
Curtis Peterson, Superintendent, Lincoln Leather Company, 2nd & Chestnut Street, Reading, Pennsylvania.

Joseph E. Steker, 3728 North Fratney Street, Milwaukee 12, Wisconsin.
Kyohei Suzuki, Ibaraki University, Mito City, Japan.
Mauricio Szerer, c/o Greenfield, Carrera 52 No. 70-139, Barranquilla, Colombia, S. A.

Changed to Associate from Student Membership

Fred Klimple, 162 Fair Street, Paterson, New Jersey.

Student Membership

Khatchig M. Darakdjian, 288 De Kalb Avenue, Brooklyn 5, New York.
Russell P. Doyle, 95 Andrews Street, Lowell, Massachusetts.
Donald E. Finegold, 77 Livingstone Avenue, Lowell, Massachusetts.
Robert F. Fulton, 23 Elise Avenue, Dracut, Massachusetts.
Gerald R. Glotzbecker, 395 Clinton Avenue, Apt. 4E, Brooklyn 5, New York.
Malcolm C. Greenidge, 100 Fairmount Avenue, Chatham, New Jersey.
Herbert J. Hodus, 26 Thornton Street, Revere 51, Massachusetts.
Emanuel J. Laios, 506 W. 179th Street, New York 33, New York.
Rai-Tsing Lee, 266 Ryerson Street, Brooklyn 5, New York.
Walter H. Sauer, 395 Clinton Avenue, Apt. 4E, Brooklyn 5, New York.

BUDGET FOR 1952

	1951 Proposed	1951 Actual	1952 Proposed
GENERAL ACCOUNT: INCOME			
Dues	$ 8,700.00	$ 8,827.53	$10,000.00
Interest on United States Bonds	653.00	725.00	725.00
By-Laws and Methods	175.00	117.90	——
Annual Meeting	——	——	——
Directory	450.00	495.49	600.00
	$ 9,978.00	$10,165.92	$11,325.00
GENERAL ACCOUNT: EXPENSE			
Executive Secretary's Salary	$ 3,500.00	$ 3,569.59	$ 4,000.00
Secretary's Office Expense	1,000.00	794.92	1,000.00
Annual Meeting	——	——	1,000.00
Committee Work	500.00	16.68	100.00
Council Meeting	100.00	176.17	200.00
Auditing	100.00	100.00	100.00
Printing Methods and By-Laws	500.00	130.00	1,000.00
Printing Directory	500.00	521.50	600.00
Reserve for Uncollectible Accounts	200.00	255.00	300.00
Winheim Award	100.00	100.00	——
	$ 6,500.00	$ 5,663.86	$ 7,400.00
Surplus on General Accounts	$ 3,478.00	$ 4,502.06	$ 3,925.00
JOURNAL ACCOUNT: INCOME			
Advertisements	$10,000.00	$10,319.32	$11,000.00
Subscriptions	3,500.00	4,112.06	4,500.00
Journals, Volumes, Reprints, Sold	2,000.00	3,342.38	3,000.00
Dues, S.L.T.C. Difference	600.00	643.25	500.00
	$16,100.00	$18,417.01	$19,000.00

JOURNAL ACCOUNT: EXPENSE			
Printing and Publishing	$15,000.00	$13,741.94	$16,000.00
Printing Reprints	2,300.00	1,751.85	2,000.00
Copyright, Insurance, Storage	500.00	456.00	500.00
Abstracts and Translations	275.00	208.77	300.00
Editor's Salary	900.00	900.00	900.00
Office and Misc. Expense (Editor)	600.00	502.92	600.00
	$19,575.00	$17,561.48	$20,300.00
Difference on Journal Account	$ 3,475.00 *(Deficit)*	$ 855.53 (Surplus)	$ 1,300.00 *(Deficit)*

Status of the Association as of February 1, 1952

MEMBERS:				
Active	430		New in 1951	79
Associate	356		Lost in 1951	75
Student	7			
	793		Gain	4
SUBSCRIBERS:				
Domestic	88		New in 1951	102
Foreign	186		Lost in 1951	121
	274		Lost	19
MUTUAL MEMBERS (S.L.T.C.)	106		Lost in 1951	56
EXCHANGE SUBSCRIPTIONS:				
Domestic	13			
Foreign	41		Increase over 1951	4
Canadian	2			
	56			
COPIES TO ADVERTISERS:	93		Lost in 1951	1
TOTAL JOURNAL Circulation	1,322		Decrease in 1951	68

Circulation Breakdown

	United States	Foreign	Canadian	Total
Active Members	362	43	25	430
Associate Members	297	37	22	356
Student Members	7	—	—	7
Mutual Members	—	106	—	106
Subscribers	82	186	6	274
Exchange	13	41	2	56
Advertisers	93	—	—	93
	854	413	55	1,322

Members Breakdown

	Active	Associate	Student*	Total
United States	362	297	7	666
Canada	25	22	—	47
Foreign	43	37	—	80
	430	356	7	793

Members Breakdown

	Active	Associate	Student	Total
Maine	—	1	—	1
New Hampshire	6	4	—	10
Vermont	—	—	—	—
Massachusetts	44	51	1	96
Rhode Island	—	2	—	2
Connecticut	4	4	—	8
New York	56	48	6	110
New Jersey	49	44	—	93
Pennsylvania	52	45	—	97
Delaware	12	7	—	19
Maryland	9	7	—	16
Washington, D. C	7	1	—	8
Virginia	11	1	—	12
West Virginia	2	3	—	5
North Carolina	3	2	—	5
South Carolina	—	—	—	—
Georgia	3	2	—	5
Florida	—	1	—	1
Kentucky	1	—	—	1
Tennessee	7	2	—	9
Alabama	—	—	—	—
Mississippi	—	—	—	—
Ohio	17	9	—	26
Indiana	1	2	—	3
Illinois	23	25	—	48
Michigan	8	2	—	19
Wisconsin	31	21	—	52
Minnesota	3	1	—	4
Iowa	—	2	—	2
Missouri	9	6	—	15
North Dakota	—	—	—	—
South Dakota	—	—	—	—
Nebraska	—	—	—	—
Arkansas	—	—	—	—
Louisiana	—	—	—	—
Oklahoma	—	—	—	—
Texas	—	—	—	—
Montana	—	—	—	—
Idaho	—	—	—	—
Wyoming	—	—	—	—
Colorado	—	—	—	—

New Mexico	—	—	—	—
Arizona	—	—	—	—
Utah	—	—	—	—
Nevada	—	—	—	—
Washington	1	—	—	1
Oregon	—	—	—	—
California	3	4	—	7
	362	297	7	666

Foreign Members Breakdown

	Active	Associate	Total
Denmark	1	—	1
Israel	1	—	1
India	5	1	6
Cuba	2	2	4
Belgium	1	2	3
Brazil	4	3	7
South Africa	1	1	2
Switzerland	2	1	3
France	2	2	4
Norway	1	1	2
Italy	—	1	1
Argentina	4	5	9
Mexico	2	1	3
Greece	1	1	2
England	2	—	2
Germany	—	2	2
Rhodesia	1	—	1
Philippines	2	—	2
Australia	—	1	1
Peru	—	2	2
Paraguay	—	1	1
Sweden	1	3	4
Uruguay	—	1	1
Chile	2	—	2
New Zealand	1	2	3
Ecuador	1	—	1
Turkey	2	2	4
Japan	4	1	5
Colombia	—	1	1
	43	37	80

Exchange List Breakdown

United States	Foreign	Canadian	Total
13	41	2	56

Advertisers — Free Copies

United States	93

S.L.T.C. Mutual Members Breakdown

England	82	Belgium	2
Australia	4	Portugal	1
Sweden	3	Erie	2
Ireland	3	Pakistan	1
Scotland	3	Egypt	2
South Africa	2		
Sudan	1	Total	106

Foreign Subscribers Breakdown

Israel	1	Malaya	1
Australia	12	Chile	1
Italy	11	Siam	1
Argentina	5	England	4
India	9	New Zealand	1
Portugal	2	Spain	6
Germany	14	Scotland	1
Russia	10	Japan	17
Switzerland	4	Turkey	1
Belgium	4	Roumania	2
Sweden	10	Indonesia	3
Holland	8	Finland	6
Norway	3	Yugoslavia	3
Hungary	3	China	1
Mexico	5	Panama	1
South Africa	2	Colombia	1
France	20	Uruguay	1
Denmark	2	Wales	1
Brazil	8		
Costa Rica	1		186

United States Subscribers Breakdown

New York	18	Oregon	1
Delaware	4	Connecticut	1
Massachusetts	7	Missouri	2
Illinois	4	Washington, D. C.	3
Minnesota	3	Wisconsin	2
Pennsylvania	8	Washington	1
Maryland	1	Alabama	1
New Jersey	5	Florida	1
California	7	Kentucky	1
Ohio	3	Michigan	4
Georgia	1	Iowa	1
Northa Carolina	1		
Texas	2		82

Canadian Subscribers 6

REPORT OF THE TECHNICAL COMMITTEES

GIVEN AT FEB. 27th COUNCIL MEETING

First I have to report some matters pertaining to the International Union of Leather Chemists Societies. Mr. Kay sent M. Queroix a copy of Federal Specification KK-L-311 in connection with the International Commission for Tannin Analysis. We have no report on the activities of the International Commission for Tannin Analysis and Leather Analysis because of the shortage of time since setting up these Commissions.

I have received a letter from Mr. Harvey, the Secretary of the International Union, containing an invitation to hold the next 1953 Leather Conference in Barcelona, Spain.

The following is a report on the activities of our Technical Committees.

VEGETABLE LEATHERS.

Nothing to report.

MINERAL LEATHERS

Seligsberger's committee has completed its work on the ammonia method for the determination of total sulfates in chrome leather. This report will be submitted for publication in the journal.

PHYSICAL AND MECHANICAL PROPERTIES

Nothing to report.

PREPARATORY TANNING OPERATIONS

Merrill has forwarded drafts of methods for our Methods Booklet. This covers beamhouse materials and fats and oils. We must obtain the consent of the American Oil Chemists Association to reprint some of their methods. The Secretary was requested to obtain this permission.

NEW ANALYTICAL TECHNIQUES

Nothing to report.

TANNERY PRACTICE

Nothing to report.

STANDARDS AND SPECIFICATIONS

Telander is meeting with the Federal Specifications Committee in Washington very shortly and will furnish a report of their findings.

LEATHER FINISHES

We have the minutes of Mr. McKee's committee meeting of November 8th in Philadelphia. We shall request him to condense this material and then submit it for publication.

H. G. TURLEY,
Technical Committees Coordinator.

A Study of the Bond Forces Involved in Chrome Tannage

By S. G. SHUTTLEWORTH

SUMMARY

The multifunctional character of collagen protein makes possible the operation, in chrome tanning, of electrovalent or salt links, coordination of amino groups to chromium, coordination of carboxy groups to chromium, residual valency forces, and hydrogen bonds, and support can be found in the literature for the importance of each of these types of bond. In order to clarify the position, exchange resins of different functional types have been tanned in comparison with hide powder by eighteen chromium complexes of widely differing charge and composition. The results show that the chief mechanism of chrome tannage is the coordination of the carboxy groups of the protein side chains to chromium, and that this mechanism is not determined by the charge on the complex, but by the number and stability of the ligands occupying the available coordination positions on the chromium atoms in the complex. In the case of monodendate acidic ligands this stability is in the inverse order of the dissociation constant of the ligand, the main carboxy groups of protein side chains thus being able to displace formate but not acetate. The stepwise nature of coordination is discussed, as well as the general principles of "masking agents."

INTRODUCTORY

The multifunctional character of collagen protein makes it possible to visualise a variety of bond forces in chrome tannage. These are:

(a) *Electrovalent or Salt Links* involving purely coulombic attraction between oppositely charged ions.

(b) *Coordinate Bonds* involving shared electron pairs. In the case of chromium complexes these are stable bonds not broken by elevation of temperature.

(c) *Residual Valency Forces* or Van der Waal's forces, due to minor electrostatic charges.

(d) *Hydrogen Bonds* which are intermediate in strength between (b) and (c) and are due to the high density of charge on the nucleus of the hydrogen atom.

Stiasny and Pakkala [1] have shown that chromium is fixed from chrome tannin solutions by such compounds as activated charcoal, alumina and kieselguhr. Elöd and Shachowskoy [2] consider that the ability of chrome tanning compounds to convert polyvinyl alcohol into a water insoluble compound shows that even the OH groups of the protein cannot be disregarded as points of attachment. Gustavson [3] has stressed the importance of the charge on the chromium complex, and has endeavoured to prove [4] that

anionic chromium complexes are attracted to the positively charged amino groups present in collagens while the cationic complexes are attracted to the negatively charged carboxy groups. The electrovalent link is thus held to be an important preliminary step in chrome tannage, to the extent that a change from cationic to non ionic complexes induces a drastic reduction in chrome fixation. Hudson [5] and Küntzel and Riess [6] regard this type of link as a reinforcing factor.

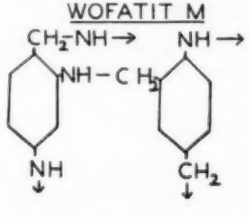
On the other hand, Stiasny [7] and Stiasny and Lochmann [8] do not consider that the charge on the complex as such is an important factor in chrome tanning, but that the determining factor is the stability of the groups occupying the available coordination positions on the chromium atoms. The writer has carried out an exhaustive study of the theory of chrome tanning [9] and has concluded that, while the presence of salt links and residual valence forces cannot be disregarded, they do not account for the high thermal stability of chrome tanned leather, which is believed to be due to bridge formation by olated chromium complexes coordinately linked to the carboxy groups of the protein network.

The object of the present paper is to compare the fixation of a wide variety of chromium complexes on hide powder and on exchange resins of the R - SO_3Na, R - COONa, and R - NH_3Cl categories, in order to ascertain the relative importance of the various types of the bond involved in chrome tanning.

Experimental

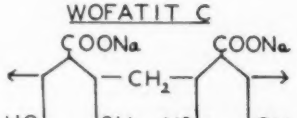
The exchange resins selected for the investigations were:-

(a) WOFATIT M

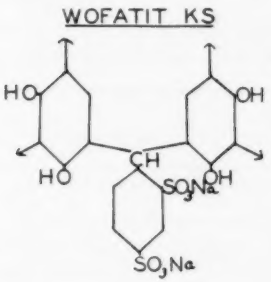


This was saturated with HCl, washed and dried.

(b) WOFATIT C



(c)



The chromium complexes were:-

(a) $\left[Cr_2(H_2O)_6(OH)_2SO_4\right]^{++} + SO_4^{=}$ A salt and organic acid free chrome tanning powder made up at 140 g/l, boiled one hour, and aged 3 months. Analysis of chromium, sulphate (total and coordinated) basicity, charge, and degree of olation, gave approximately the above composition.

(b) $\left[Cr(H_2O)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{-} + K^+$ Obtained by ageing pure trans potassium diaquo dioxalato chromiate in aqueous solution to convert it to the cis form (See Burley [10]).

(c) $\left[Cr\begin{pmatrix}COO\\|\\COO\end{pmatrix}_3\right]^{\equiv} + 3K^+$ Obtained by dissolving the analytically pure salt.

(d) $\left[Cr_2(H_2O)_6(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}\right]^{++} + 2SO_4^{=} + 2Na^+$

(e) $\left[Cr_2(H_2O)_4(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{o} + 4na^+ + 2SO_4^{=}$

(f) $\left[Cr_2(H_2O)_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}_3\right]^{-} + 6Na^+ + 2SO_4^{=}$

Complexes (d), (e) and (f) were obtained by boiling complex (a) at 140 g. Cr_2O_3 per liter with the stoichiometric proportions of sodium oxalate and ageing the solution for one week before use. The compositions were checked by potentiometric titration, by spectrophotometric curves and by exchange resins, as described later.

(g) $\left[Cr_2(H_2O)_6(OH)_2SO_3\right]^{++} + 2Na^+ + 2SO_4^=$

(h) $\left[Cr_2(H_2O)_4(OH)_2(SO_3)_2\right]^{o} + 2Na^+ + 2SO_4^=$

Complexes (g) and (h) were made by warming complex (a) at 140 g/l. Cr_2O_3 with stoichiometric proportions of sodium sulfite to dissolve the latter (boiling avoided to obviate loss of SO_2), maintaining at 37° C for 24 hours, and ageing for 1 week before use. The compositions were checked by potentiometric titration with HCl, by spectrophotometer, and by exchange resin analyses.

(i) $\left[Cr_2(H_2O)_5(OH)_2(HCOO)_3\right]^{+} + 4Na^+ + HCOO^- + 2SO_4^=$

(j) $\left[Cr_2(H_2O)_4(OH)_2(HCOO)_4\right]^{o} + 8Na^+ + 4(HCOO)^- + 2SO_4^=$

These two complexes were formed by warming complex (a) at 140 g/l. Cr_2O_3 with stoichiometric proportions of sodium formate to dissolve the latter, maintaining at 37° for 24 hours, and ageing for 1 week before use. The compositions were arrived at by potentiometric titration with HCl, by spectrophotometer, and by exchange resin analyses. Complex (j) had somewhat less coordinated formate than indicated in the formula given, and contained about 10% of positively charged ions.

(k) $\left[Cr_2(H_2O)_3(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(HCOO)_3\right]^{-} + 6Na^+ + (HCOO)^- + 2SO_4^=$

(l) $\left[Cr_2(H_2O)_3(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(HCOO)_3\right]^{-} + 8Na^+ + 4(HCOO)^- + 2SO_4^=$

These two complexes were formed by boiling complex (a) at 140 g/l. Cr_2O_3 with one mole per Cr_2O_3 of sodium oxalate, adding stoichiometric proportions of sodium formate to the hot solution, maintaining at 37° C for 24 hours, and ageing for 1 week before use. The compositions were arrived at by potentiometric titration with HCl, by spectrophotometer, and by exchange resin analyses. Complex (k) contained about 8 per cent less formate in the

coordinated form than indicated by the formula, while complex (l) contained about 5 per cent more complex bound formate than indicated.

(m) $\left[Cr_2(H_2O)_6(OH)_2\,(CH_3COO)_4 \right]^{o} + 4Na^{+} + 2SO_4^{=}$

(n) $\left[Cr_2(H_2O)_5(OH)_2 \begin{pmatrix} COO \\ | \\ COO \end{pmatrix} (CH_3COO)_3 \right]^{-} + 6Na^{+} + (CH_3COO)^{-}2SO_4^{=}$

(o) $\left[Cr_2(H_2O)_5(OH)_2 \begin{pmatrix} COO \\ | \\ COO \end{pmatrix} (CH_3COO)_3 \right]^{-} + 8Na^{+} + 3(CH_3COO)^{-}2SO)_4^{=}$

These acetate and mixed acetate plus oxalate complexes were prepared and analysed in a similar manner to the formate complexes (i), (j), (k) and (l) above. The complex (m) contained about 10 per cent less coordinated acetate, while the complex (o) contained about 5 per cent more acetate than that indicated by the structures given.

(p) $\left[Cr_2(H_2O)_4(OH)_2 \begin{pmatrix} COO \\ | \\ COO \end{pmatrix} SO_3 \right]^{o} + 4Na^{+} + 2SO_4^{=}$

(q) $\left[Cr_2(H_2O)_2(OH)_2 \begin{pmatrix} COO \\ | \\ COO \end{pmatrix} SO_3 \right]^{=} + 6Na^{+} + 2SO_4^{=}$

(r) $\left[Cr_2(H_2O)_2(OH)_2 \begin{pmatrix} COO \\ | \\ COO \end{pmatrix} (SO_3)_2 \right]^{=} + 6Na^{+} + 2SO_4^{=}$

These mixed oxalate sulfite complexes were prepared by boiling complex (a) at 140 gms. Cr_2O_3/litre with stoichiometric proportions of sodium oxalate, adding stoichiometric proportions of sodium sulfite to the hot solution, maintaining at 37°C for 24 hours, and ageing for 1 week before use. The compositions were checked by potentiometric titration with HCl, by spectrophotometer, and by exchange resin. In the case of (q) and (r) about 15 per cent of the added sulfite could be titrated with HCl after formation of the complexes.

Characterisation of the Complexes

A detailed account of the characterization of each of the above complexes would be tedious in the present context. Briefly the method involved is the following:-

Degree of Olation. Potentiometric titration of 5 ccs. of the complex in 100 ccs. of water with $\frac{N}{2}$ HCl, corrected by a blank on water, gives the degree of olation of the OH groups.

Total OH Groups. The pH values of all the diol complexes excepting the unmasked sulfate complex (a), lay between 4.33 and 6.0 including the fully coordinated oxalate and sulfite complexes. Most of them had very little uncoordinated salt, so that any marked increase in basicity arising from alkali contributed by the added buffer salts should have shown a corresponding liberation of acid and thus a lower pH value. Thus it was possible to deduce no change in OH content.

Coordinated Groups. Potentiometric titration as for the degree of olation, gives both degree of olation plus uncoordinated weak acid groups. In most cases potentiometric titration with acid showed no titratable groups, and it was thus assumed that olation was complete for all the complexes. Hence the acid absorbed in the remaining cases could be regarded as indicative of uncoordinated weak acid groups. Spectrophotometric curves were used to establish the monodendate or bidendate character of the attachment (see later).

Charge. This was determined by the exchange resin technique advocated by Gustavson [4].

H_2O Groups. These were calculated.

Tanning Method

1 gm. portions of hide powder or the appropriate resin were placed in 100 cc. Erlenmeyer flasks, covered with 50 ccs. of water, and maintained at 37°C for 1 hour. 10 cc. portions of each of the 18 chromium complexes at 140 gms. per litre Cr_2O_3 were added to the Erlenmeyers and tannage carried out for 3 hours at 37°C. The resins or hide powder were filtered off, each washed four times with 50 cc. portions of cold water using a Buchner to expedite filtration and analysed.

For shrink temperature determinations, 10 cm x 1 cm. portions of limed, delimed, bated sheepskin were used instead of hide powder or resin, the tanning conditions being otherwise the same as before. The shrink temperatures were measured by the "shock treatment" method advocated by Gustavson [3], involving a preliminary determination by the normal method, followed by a second determination involving the minimum time of heating of the sample. This was found to be particularly necessary for the sulfite complexes, where prolonged heat caused a considerable rise in shrink temperature, due possibly to evolution of SO_2.

Results

Table 1 gives a summary of the results obtained for these tannages.

TABLE I

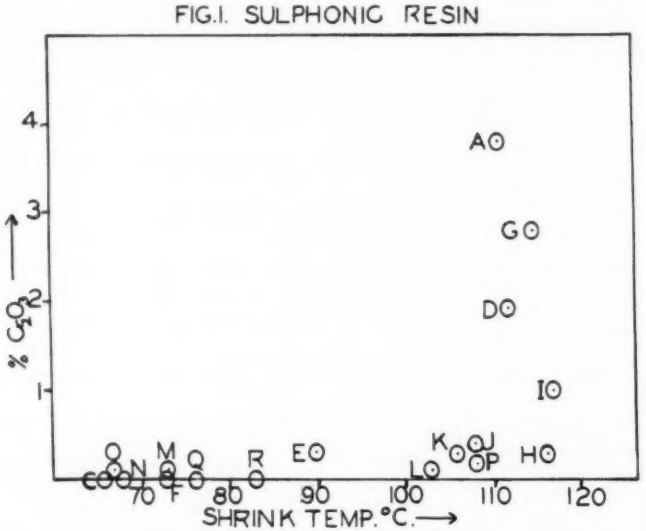
Chrome Uptake by Resins and Hide Powder.

	Approximate Formula of Complex	Chrome Uptake (as Cr_2O_3)				Shrink Temperature
		R-NH_3Cl	RCOONa	RSO_3Na	Hide Powder	
(a)	$\left[Cr_2(OH)_2SO_4\right]^{++}$	0.8%	4.0%	3.8%	8.1%	111°C.
(b)	$\left[Cr\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{-}$	4.7%	0.6%	0.0%	1.3%	82°C.
(c)	$\left[Cr\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{=}$	4.6%	0.0%	0.0%	0.1%	66°C.
(d)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}\right]^{++}$	2.3%	3.6%	1.9%	11.7%	112°C.
(e)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{0}$	3.1%	1.6%	0.3%	12.1%	90°C.
(f)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}_2\right]^{=}$	4.0%	0.3%	0.0%	6.9%	73°C.
(g)	$\left[Cr_2(OH)_2SO_2\right]^{++}$	0.1%	3.0%	2.8%	10.6%	115°C.
(h)	$\left[Cr_2(OH)_2(SO_3)_2\right]^{0}$	0.2%	2.4%	0.3%	22.0%	116°C.
(i)	$\left[Cr_2(OH)_2(HCOO)_2\right]^{+}$	0.6%	3.6%	1.0%	6.9%	117°C.
(j)	$\left[Cr_2(OH)_2(HCOO)_4\right]^{0}$	1.0%	3.0%	0.4%	5.9%	108°C.
(k)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(HCOO)_2\right]^{-}$	2.9%	2.0%	0.3%	6.7%	106°C.
(l)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(HCOO)_2\right]^{-}$	3.0%	1.8%	0.1%	6.4%	103°C.
(m)	$\left[Cr_2(OH)_2(CH_3COO)_4\right]^{0}$	0.0%	0.4%	0.1%	2.2%	72°C.
(n)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(CH_3COO)_2\right]^{-}$	1.8%	0.3%	0.0%	2.7%	68°C.
(o)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(CH_3COO)_2\right]^{-}$	1.8%	0.2%	0.0%	2.3%	67°C.
(p)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}SO_3\right]^{0}$	1.8%	2.1%	0.2%	19.1%	108°C.
(q)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}SO_3\right]^{=}$	2.6%	0.2%	0.0%	6.6%	76°C.
(r)	$\left[Cr_2(OH)_2\begin{pmatrix}COO\\|\\COO\end{pmatrix}(SO_3)_2\right]^{=}$	1.5%	0.2%	0.0%	15.8%	83°C.

Relation Between Charge and Chrome Tannage

(a) *Positively Charged Complexes*

Fig. 1. shows the relation between the sulfonic resin fixation (positively charged complexes) and shrink temperature. It is apparent that the charge on the complex is unimportant in so far as thermal stability of leather is concerned, and must be regarded as of minor significance. A comparison of Figs. 1 and 4 shows that this is equally true in regard to chrome fixed by hide powder.



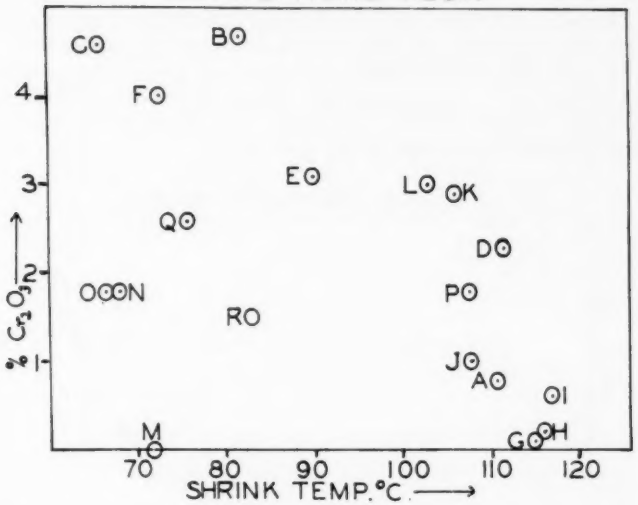
(b) *Neutral Complexes.*

Many of the uncharged complexes gave high fixations on the carboxy resin and hide powder, and high shrink temperatures resulted from pelt tanned with them.

(c) *Negatively Charged Complexes.*

Fig. 2. shows the relation between the amino resin fixation (negatively charged complexes) and shrink temperature. It is again apparent that the charge on the complex is unimportant, and a comparison of Figs. 2 and 4 shows that this is equally true in regard to chrome fixed to hide powder. It is particularly interesting to note that potassium trioxalate chromate, although carrying three negative charges per Cr, and giving the highest fixation on the amino resin, possessed no affinity for hide powder.

FIG. 2. AMINO RESIN



It is evident that collagen protein, being able to satisfy its coulombic forces internally without the aid of extraneous ions, does not bind chromium complexes by single electrovalent links unless reinforced by other factors such as large particle size giving rise to multiple points of attachment. Nor is the charge, as such, a determining factor as to whether or not a complex will coordinate with the carboxy groups of resin or protein.

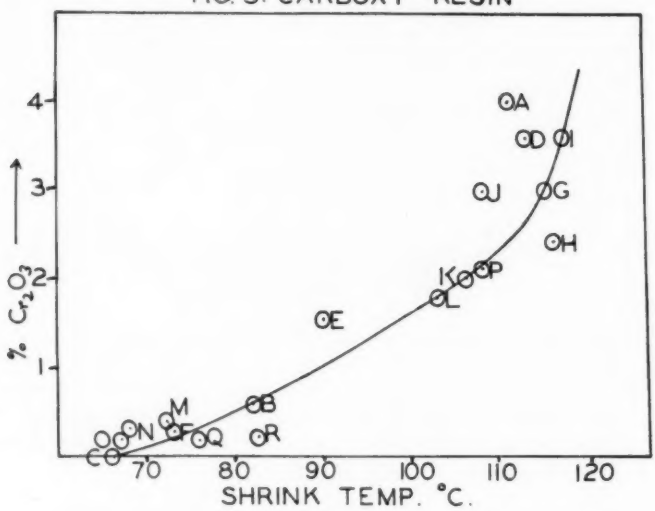
Residual Valency Forces

The term adsorption is generally used to connote a type of combination which is regarded as the result of residual valency forces, small in individual effect, but quite effective in total. Such forces are more likely to account for chrome fixation where large and semi colloidal complexes are used to tan, such as highly basic chromium sulfate complexes close to the precipitation point. Evidence of this type of fixation can be found in Table I. Many positively charged or uncharged complexes give fixations on the amino resin. while there are many cases of high hide powder fixations which cannot be explained by the total resin fixations. The sulfite and oxalato sulfito complexes are particularly noteworthy in this respect.

However there are numerous examples of compounds other than chromium complexes which tan by residual valency and hydrogen bond forces, and none of these gives the high thermal stability to pelt which is characteristic of chrome tannage. It is evident that such weak bond forces are easily

broken by heat. An excellent confirmation of this is the monooxalato disulfito dihydroxy chromiate (r) which gave a hide powder fixation of 15.8% and yet was only able to impart to pelt a shrink temperature of 83°C. The lack of correlation between hide powder fixation and shrink temperature shown in Fig. 4 can be accounted for by this type of weakly bound chromium. If this type of chrome fixation was a serious factor in thermal stability, some correlation should be apparent in Fig. 4.

FIG. 3. CARBOXY RESIN

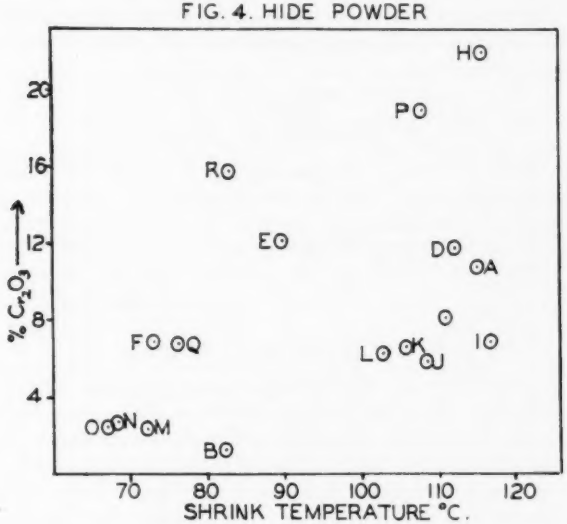


It is evident that fixation of chromium complexes by residual valency forces should be regarded as a filling action rather than as the chief mechanism of chrome tannage, which must differ fundamentally from that of alum or vegetable tannage, as evidenced by the relatively high thermal stability of chrome tanned leather.

Coordination of Amino Groups

It has already been shown by the writer[9] that amino groups of the types found in collagen protein do not coordinate appreciably with basic chromium complexes under the conditions of normal chrome tannage in aqueous solution. Fig. 2. gives further proof of this, as no correlation between amino resin fixation and shrink temperature appears to exist. An examination of Table 1 shows that all the complexes which had no appreciable affinities for the carboxy resin were also unable to enhance appreciably the shrink temperature

FIG. 4. HIDE POWDER



of raw pelt, even though some of them gave high amino resin and hide powder fixations.

Coordination of Carboxy Groups

The writer has shown[11] that the affinity of monodendate acidic ligands for coordination with chromium is in the inverse order of their dissociation constants, and that this explains some of the properties of masking compounds in chrome tannage. Bjerrum[12] has demonstrated a similar relationship between dissociation constants and coordination tendency for silver and mercury complexes, i. e. log $K_{Ag}+$ shows a linear relationship when plotted against log K_H+ for the ligand. Another way of stating this is that the tendency of an ion to coordinate with metal ions is in the same order as its tendency to coordinate with hydrogen ions. In solution the metal and hydrogen ions (H_3O+) are coordinated to water and the ligand can be regarded as competing with water in both cases. In order to place the carboxy groups of collagen protein in the correct order of affinity for chromium, it is essential to know their pK values. According to Braybrooks[13] the main acid residues are aspartic acid (2.94%) and glutamic acid (5.09%), which have pK values of 3.76 and 4.2 respectively. After due allowance for the Donnan effect, Peters and Speakman[14] calculate the average pK value of the sidechain carboxy groups of wool as 4.3. Collagen protein, having a somewhat higher proportion of the stronger aspartic acid, should have a pK value of slightly

less then that observed for wool. The carboxy resin used in Table 1 can be expected to have a pK value of approximately 4.0. Table 2 gives a list of significant pK values:-

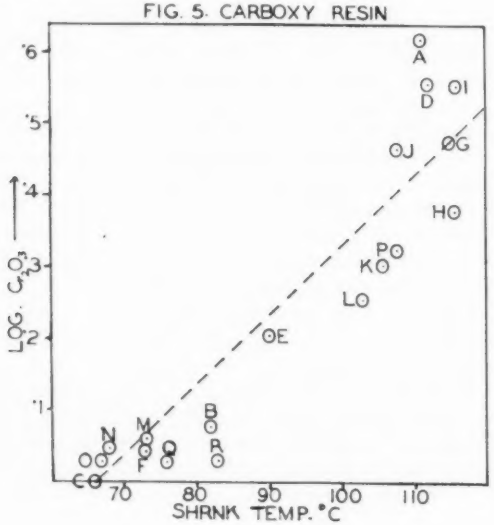
TABLE 2

pK Values of Various Ligands

Ligand	pK Value
Formic Acid	3.7
Aspartic Acid (α-COOH)	3.76
Wofatit C (3.5 dihydroxy benzoic acid)	4.0 (approx.)
Glutamic Acid (α-COOH)	4.2
Wool Protein	4.3
Acetic Acid	4.7
Sulphurous Acid	1.7 and 5.5

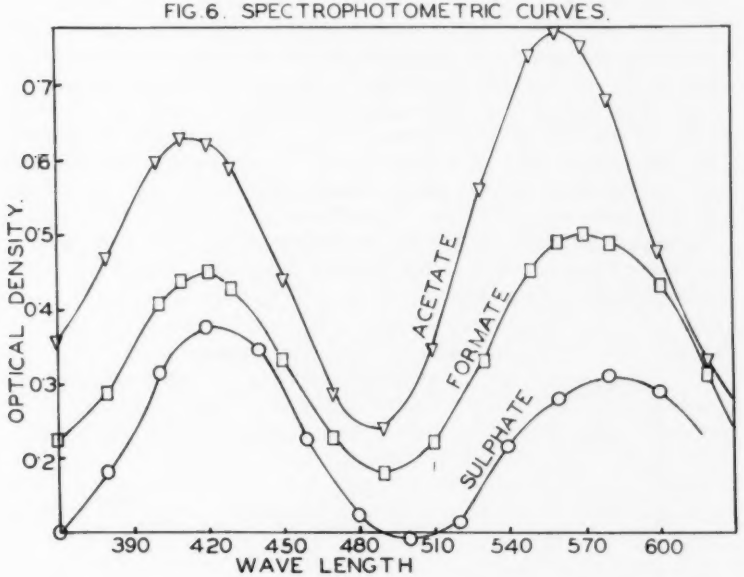
It is at once apparent that the two main carboxy groups of collagen protein can be expected to compete favourably with formic acid in chromium formate complexes, but unfavourably with acetic acid in chromium acetate complexes. This explains the different behaviour of these two types of complex shown in Table I, the formate complexes giving good fixations on both carboxy resin and hide powder and leather with high thermal stability, while the acetate complexes show poor tanning power. This difference in affinity is demonstrated in Fig. 6, which shows the spectrophotometric curves of formate and acetate complexes.

FIG. 5. CARBOXY RESIN



The writer has pointed out previously[9] that there appear to be no cases on record where coordination between carboxy groups and basic chromium sulfate complexes do not occur under conditions similar to chrome tannage and that therefore it must be accepted that stable coordination compounds between protein carboxy groups and chromium ions do occur in chrome tannage. Fig. 3 provides positive proof of the correlation between the fixations of eighteen widely different chromium complexes on the carboxy resin and the thermal stability of leathers tanned by these complexes. In view of the correlation between the log of the hide powder fixation and the shrink temperature found by Pressley et al[15], the results have been replotted in Fig. 5 on a logarithmic basis. It should, however, be pointed out that Pressley's results were obtained on a single complex.

FIG. 6. SPECTROPHOTOMETRIC CURVES.



Weir[16] has divided thermal stability into entropy of activation and free energy terms, and considers that bridging of protein chains increases the former, while the latter is a steric hindrance phenomenon related to size of particle attached. The bridge concept has been supported by the writer with many arguments[9], and needs no further comment at this stage.

In Figs. 3 and 5 variations from the correlation curves may be due to:-

(a) Varying particle sizes.

(b) Failure of very large particles to penetrate the resin network [17].

(c) Varying amounts of bridging of protein chains not entirely related to carboxy resin fixation.

(d) Reinforcing effects on shrink temperature of chromium attached by other than coordination bonds.

In view of the widely different types of complex used, and the interference of the above effects, the correlation between carboxy resin fixation and thermal stability is remarkable and provides striking proof that the important factor in chrome tannage is the coordination of protein carboxy groups to chromium complexes. This proof is reinforced by the absence of correlation in Figs. 1, 2 and 4, which shows that the coordination of carboxy groups is the main mechanism in chrome tannage.

Theoretical Considerations of Masking

It should be noted that some of the eighteen complexes used involve levels of masking which would be uneconomic in commercial practice. The proportions of masking agents used in commercial tanning are such that the complexes are generally cationic while very large complexes give rise to penetration difficulties, so that the complexes used in practice are unlikely to give much coulombic or residual valency fixation, and coordination to carboxy groups probably accounts for the bulk of chrome fixation in normal tannage.

Bjerrum [18] has demonstrated the stepwise coordination of monodendate ligands to chromium and gives the following dissociation constants of thiocyanate complexes at 50°C:-

TABLE 3

Stepwise Affinity of Monodendate Ligands

Complex	Dissociation Constant	Affinity in Calories
$\left[Cr(CNS)\right]^{++}$	32.8	3710
$\left[Cr(CNS)_2\right]^{+}$	17.5	1840
$\left[Cr(CNS)_3\right]^{0}$	4.56	970
$\left[Cr(CNS)_4\right]^{-}$	1.93	420
$\left[Cr(CNS)_5\right]^{=}$	0.81	−130
$\left[Cr(CNS)_6\right]^{\equiv}$	0.41	−570

This effect does not show a sharp change in gradation of affinity at the point where the charge changes in sign as would be required in Gustavson's explanation of the neutral salt effect in chrome tannage [3]. Burkin [19] points out that these stepwise differences in coordination affinity are due to composite causes, partly electrostatic, party statistical, and partly the effects of the ligands on each other and on the electron orbitals used for bond formation. It is apparent that the so called "masking effect" in chrome tannage is related to the number of ligands occupying the available coordination positions of the chromium complex, and the relative stability of the association.

The problem of the mondendate masking agents such as formate and acetate has already been discussed in the preceding section. It should be noted in Table 1 that the formation of negatively charged complexes with formate and acetate ions was facilitated by the addition of one mole of oxalate per Cr_2O_3, and that the dioxalato chromium complex was a much better tanning agent than the corresponding tetraacetato complex. The implication is that the inhibiting effect on further coordination is not as great when some of the available coordination positions are occupied by stable oxalate rings, as when occupied by stable monodendate ligands. This may be a steric factor, or may be related to the effect of oxalato masking on the electron orbitals of the chromium atom.

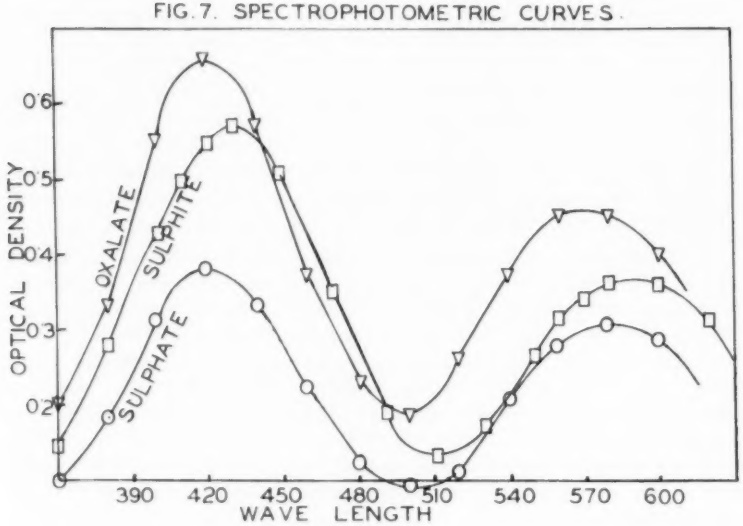
The bidendate ligands such as polybasic organic acids or α hydroxy acids can be divided into two categories:-

(a) Bidendate ligands forming 5, 6 or 7 membered rings, giving no increment in number of chromium atoms per mole, and occupying available coordination positions with stability enhanced by the additional states of resonance provided by the ring structure. The damping effect on this resonance caused by interposing CH_2 groups in the ring, plus additional strain, appears to be the reason for decreasing stability with increasing size of ring.

(b) Long chain polydendate ligands which enhance the size of the chromium complex and increase chrome fixation in leather by linking chromium atoms together. It is suggested that these non ring forming polydendate ligands can be regarded, from a stability viewpoint, as fitting into the series of mondendate ligands, with stabilities inversely proportional to their dissociation constants.

The problem of bidendate sulfate and sulfite groups is not fully solved, but it seems likely that the olated dihydroxy dichromium ions form six membered rings involving less strain than the alternative four membered rings. The difference in electron mobility of the olated chromium atoms would account for the lower stability of this diol ring as compared with the oxalate type of complex. The readiness with which sulfite ions displace sulfate ions from these complexes is accounted for by the wide differences in dissociation constants. Riess and Barth [20] have stated that sulfites tend

FIG. 7. SPECTROPHOTOMETRIC CURVES.



to form large complexes. This could be due to association between complexes, to linking of complexes together by sulfite groups, or to less of SO_2 followed by olation of the more basic complex. The spectrophotometric evidence, contained in Figs. 6 and 7 suggests that the monodendate ligands enhance the second peak (violet colour) while ring forming bidendate ligands such as oxalate enhance the first peak more strongly (green colour). This would suggest that sulfate and sulfite groups form six membered rings, the sulfite ions giving the higher absorption density on account of greater stability.

Conclusions

1. Collagen protein, being able to satisfy its coulombic forces internally, does not bind chromium complexes by coulombic attraction of single electrovalent links unless reinforced by other bonds. Nor is the charge as such, the determining factor as to whether or not a complex will coordinate with the carboxy groups of resin or protein.
2. Residual valence forces must be regarded as of minor importance in chrome tanning, capable of fixing chromium under favourable conditions, but not able to impart the high thermal stability characteristic of chrome tanned leather.
3. Further evidence confirms the view that amino groups of the types found in collagen protein do not coordinate appreciably with basic chromium

complexes in dilute aqueous solution under the conditions of chrome tannage.

4. The chief mechanism of chrome tannage is coordination of chromium to the carboxy groups of protein side chains. This reaction is not determined by the charge on the complex but by the number and stability of the groups occupying the available coordination positions on the chromium atom. The charge is one of several factors influencing ligand stability.
5. The number of occupied coordination positions is important owing to the stepwise drop in ligand affinity which is also influenced by the type of ligand.
6. The ability of protein carboxy groups to displace other ligands from chromium complexes is shown to be inversely related to the dissociation constants of the ligands, which explains why chromium formate complexes tan while chromium acetate complexes do not. The additional stability conferred by ring forming polydendate ligands and the high chrome fixation imparted by non ring forming polydendate ligands can also be anticipated from this interpretation of chrome tannage.

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The Variation of the Physical and Chemical Properties of Split and Unsplit Chrome-Tanned Leathers

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Abstract

A study was made of the variation of the physical and chemical properties over the area of a side and between sides of split and unsplit chrome-tanned upper leather. Thirty steerhides of the same tannage were used in this study. One side of each hide was split, while the other side remained unsplit.

The effect of splitting on the properties of the sides is shown. A study was made of the correlation of the results of various tests between the sides of the same hide and between the corresponding locations of the same hide. The results indicate that a high correlation exists for the physical properties between sides of the same hide. Standard deviations between blocks and between side averages for each of the tests were determined.

The results of the chemical analysis show that the chromic oxide occurs in a definite ratio to hide substance for all locations. Moisture content also shows a constant ratio to hide substance for all locations. The grease content is inversely related to the hide substance content, but does not occur in a definite ratio to the latter. The variation of the percentages of the chemical constituents is much less than that for the values obtained in the strength tests.

I. Introduction**

An intensive study on military shoe upper leather was initiated by the Office of the Quartermaster General three years ago. The purpose of this study was to improve the quality of shoe upper leather by determining the best type of tannage and also by the development of a more efficient and more scientific sampling procedure for acceptance testing. One of the first phases of this involved a detailed study of the physical and chemical properties of split chrome-tanned leathers in different locations over the area of the hide. From these results a tentative sampling procedure [1, 2] was adopted for chrome-retanned upper leather.

This sampling procedure has been applied to the testing of about 100 lots of different types of upper leather which were studied to determine the best type of tannages. In addition the properties of unsplit chrome-tanned leathers

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similar to the split chrome-tanned leathers and chrome-retanned cow and steer sides were determined to supplement the data on sampling obtained with the split chrome-tanned leather.

Of the two papers already published, the one in the Journal of Research gives the theoretical basis for the development of the sampling method and the one in the Journal of American Leather Chemists Association gives the detailed sampling procedure and some of the results of the physical tests on the split leathers. The present paper gives a detailed comparison of the results of both physical and chemical properties of the split and unsplit leathers and much of the data in detail used in the sampling study.

The split and unsplit leathers were chrome-tanned and stuffed. This tannage was selected because it is thought that the chrome tannage changes the physical properties the least and should, therefore, give the most fundamental basic data on hide and location variations.

In the selection of these leathers for study, hides were cut into two sides, one of which was split according to the procedure for making upper leather, the other remained unsplit. The split and unsplit sides were subjected to identical tanning and finishing treatments. The selection of the leathers in this way made possible the study of the correlation between sides of the same hide where the only difference is splitting.

II. Sampling Areas

The method of determining the cutting or sampling area of the sides is shown in Figure 1. The line AB was drawn parallel to the backbone line, and in such a way that minimum distance between the line AB and the backbone edge was one inch. The line BD nearest the butt drawn perpendicular to the backbone line and two inches from the root of the tail at B. The line AC nearest the head was drawn parallel to the line BD and through a point

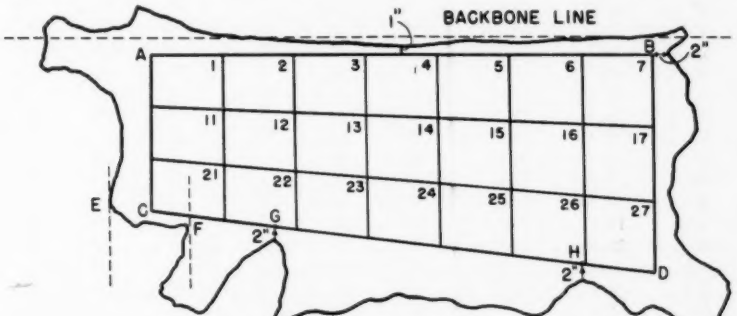


FIGURE 1.—Relation of sampling area to the side and the design used in cutting the sides into blocks.

equidistant from points E and F. The line nearest the belly was drawn through points G and H (2 inches above the highest portion of the front and rear flanks). The blocks in the sampling area were formed by drawing lines parallel to BD from points on AB placed at increments of units equal to 1/7 of the length of AB to DC, and by drawing lines from BD to AC at points on these lines placed at increments of units equal to 1/3 of their lengths. Since AC was in every instance shorter than BD the blocks in the shoulder area were smaller than those in the butt area (Figure 2). The areas of the sides together with the length of the lines AB, BD, and AC for each of the split and for the unsplit sides are given in Table 1.

TABLE 1

Areas of Original Sides and Dimensions of Test Areas
Split and Unsplit Leathers

Hide	Original Areas		Corresponding Sides Dimensions of Test Areas					
	Split	Unsplit	Split			Unsplit		
			AB	BD	AC	AB	BD	AC
	Ft²	Ft²	in	in	in	in	in	in
A	18.1	18.0	63	27	21	66	27	18
B	21.2	20.0	66	29	22	66	30	20
C	20.0	19.3	67	30	21	67	30	20
D	20.1	20.3	67	30	21.5	70	30	20
E	22.0	20.2	70	30	20.5	69	30	21
F	20.3	20.0	70.5	29	21.5	70	27	21
G	19.3	19.3	68.5	28	21	67	27	21
H	20.0	19.1	67	29.5	21	67	27	21
J	20.3	21.0	71	30.0	20.5	70	29	21
K	19.0	19.1	70	27	21	69	28	20
L	18.2	19.1	67.5	28.5	20.5	68	30	20
M	21.2	22.1	68	30.5	21.5	62	28	21.5
N	20.1	21.0	66.5	29	21	67	29	21
O	20.3	20.0	70	28.5	21	68	27.5	21
P	23.2	23.2	71	34	23	72	30	21
Q	22.2	21.2	72	31	21	72	30	20.7
R	21.2	21.0	69	31	21	70	30	21
S	22.0	21.0	69.5	32.5	22	70.3	30	20.4
T	19.3	21.0	69.5	29	20.5	68	31	22.5
U	19.4	19.1	69	28.5	21	67	28.5	20.5
V	19.3	20.1	65.5	31	21.5	66	27	21
W	21.3	23.0	69	31.5	21.5	72	30	21
X	19.2	19.3	69.5	28.5	21	70	27	21
Y	19.6	20.0	65.5	31	20.5	67	30	21
Z	20.0	19.3	66.5	29	21	66	28	21
XA	21.2	20.0	68	31.5	21	71	30	21
XB	19.4	18.3	65.5	30	21	67	29	21
XC	21.2	21.0	67.5	31	21	67	28	21
XD	19.4	17.2	66	29.5	20.5	68	27	20
XE	20.0	19.0	68	29	21	67	30	20.6
Ave.	20.3	20.1	68.1	29.8	21.1	68.2	28.8	20.7

Selection of the Test Specimens

The unsplit sides were sampled for tests by the same procedure used for the split sides described in [2]. This plan for cutting the blocks and the specimens is reproduced for the convenience of the reader of this paper in Figure 2. As in the study with the split sides, 30 sides of unsplit leather were used. The physical and chemical tests generally applicable to upper leather were applied, i. e., tensile strength, elongation, stitch tearing strength, tongue tearing strength, bursting strength, water penetration, water vapor permeability, chromic oxide, ash, hide substance, and grease.

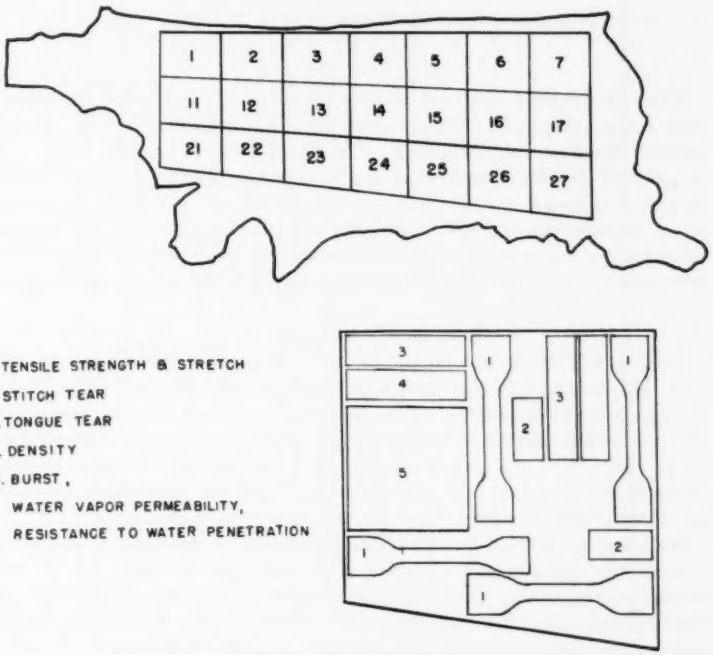

1 2 3 4 5 6 7
11 12 13 14 15 16 17
21 22 23 24 25 26 27
1. TENSILE STRENGTH & STRETCH
2. STITCH TEAR
3. TONGUE TEAR
4. DENSITY
5. BURST,
WATER VAPOR PERMEABILITY,
RESISTANCE TO WATER PENETRATION

FIGURE 2.—Design used in taking specimens from blocks.

Considerations based on the required specimen sizes for the various tests as well as on the total area of the side for the selected stock led to the adoption of the pattern of 21 blocks or positions on each side, formed by three rows and seven columns as described above and shown in Figure 2. Specimens for most of the tests were cut from each block of each of the 30 sides. Bursting strength and water resistance specimens were cut from alternate blocks only. Figure 2

shows the pattern according to which each block was cut into specimens for the various tests. It will be noticed that for all strength tests in which a directional effect may be expected, specimens were cut in two directions parallel and perpendicular to the backbone. In every block tensile strength was determined on two specimens perpendicular to the backbone. Tensile strength parallel to the backbone was determined on at least one specimen in every block and wherever size of block permitted, which was in about 50 per cent of them, tensile strength in the parallel direction was determined on two specimens.

The chemical analysis was determined on the unused portions of the blocks and on the broken tensile strength specimens.

III. Test Methods

The test methods used are described in Federal Specification KK-L-311, with a few exceptions. Water penetration was measured by the dynamic method developed by Maeser [3]. The strength tests, tensile, stitch tear, tongue tear, and burst were made in a Tinius Olsen Testing Machine [4] which, by proper adjustment of the loading range, afforded a high degree of accuracy at any required load. A special adapter was developed for use with this machine for measuring bursting strength which is described in [2]. Water vapor permeability was measured by the method developed by Kanagy and Vickers [5].

IV. Results and Discussion

Since it was impossible to publish all of the large mass of data obtained from the physical and chemical tests applied to the split and unsplit sides, averages and various studies on the data in a condensed form are given in an effort to present that which would be of the greatest usefulness. Side averages for all of the tests are given. Since there is considerable variation between blocks of the same side but fairly good uniformity between the corresponding blocks of different sides, block averages are also presented.

Statistical analyses of the data included studies of the standard deviations between the side averages. Studies of the standard deviations of the tests between corresponding blocks of the sides were found more valuable than the standard deviations between blocks of the same side. Correlation studies between the various physical test methods on a side-to-side and a block-to-block basis are also included together with the percentage coefficient of variation for the blocks between sides and for the side averages.

a. Physical Tests

The original areas and the dimensions of the test areas of the split and unsplit chrome-tanned sides are given in Table I. These values agree very well, and there is also uniformity of area and dimensions between sides of the same hide.

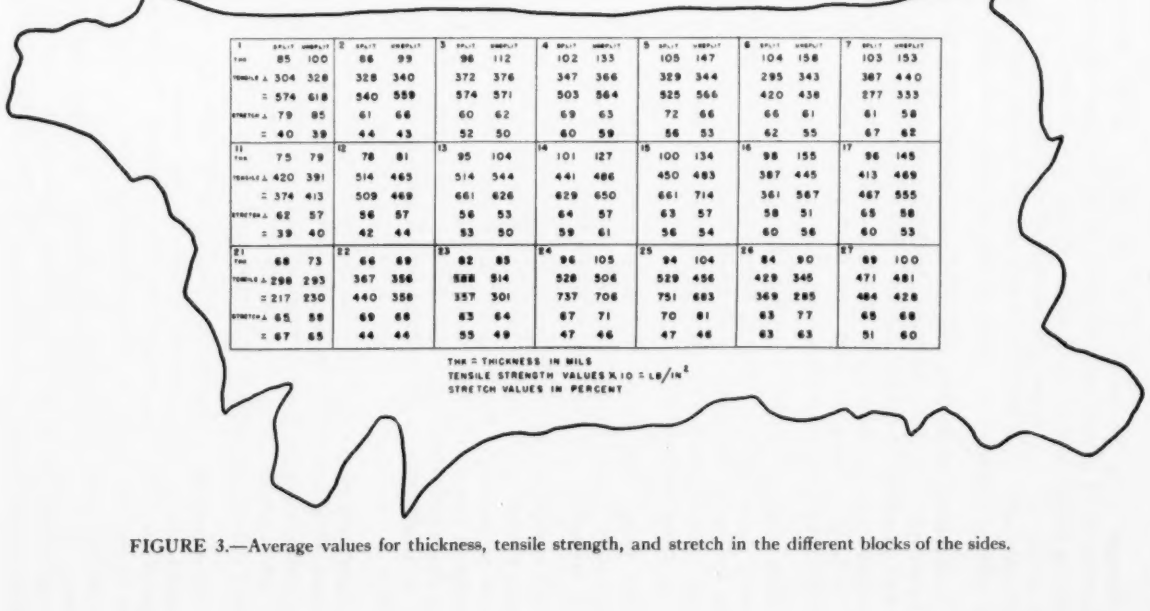


FIGURE 3.—Average values for thickness, tensile strength, and stretch in the different blocks of the sides.

Average values for thickness, tensile strength in two directions, and stretch at break in two directions for all of the blocks are given in Figure 3. From an examination of the thickness values only blocks 4, 5, 6, 7, 14, 15, 16, and 17 had any appreciable amount of the hide removed by splitting. The other split blocks are 3 to 16 mils thinner than the unsplit blocks, but the splitting amounted to little more than scraping off the flesh surfaces.

A comparison of the results of the tensile strengths shows that where the sides are split appreciably the unsplit leather is stronger than the split leather in both parallel and perpendicular directions. For the other parts of the side, the split leather in the majority of the blocks is stronger. Several locations in the belly and shoulder areas have much greater tensile strengths in the parallel than in the perpendicular directions.

Block averages for burst and stitch tear and tongue tear in the two directions of test are given in Figure 4. Burst values on the thickness basis for the split leather are for nearly every block greater than those of the unsplit leather. Burst values are greater in the middle row and belly areas than in the butt and backbone areas.

The tongue tear values approximate roughly one-half the values for stitch tear. Tongue tear and stitch tear values are higher in the shoulder and belly areas than in the butt and backbone areas.

Side averages for all of the physical tests are given in Table 2. The average tensile strength in the parallel direction is about 20 per cent higher than that in the perpendicular direction. Stitch tear in the parallel direction on the average is also greater than that in the perpendicular direction. Tongue tear shows little difference in the two directions of test. The average burst for the split leather on the thickness basis is greater than that for the unsplit leather.

Correlation of the results of the different tests on a side-to-side and a block-to-block basis for the split and unsplit sides are given in Table 3. The correlation using the block averages is higher in every case than that using the side averages. This shows the importance of sampling corresponding blocks or locations between hides in research work.

The percentage coefficients of variation of the split and unsplit blocks between sides for tensile strength, stitch tear, and tongue tear in two directions of test and bursting strength are given in Table 4. The average coefficients for the sides are of the same order of magnitude for all of the tests and for each direction of test, except for tensile strength in the parallel direction which is about 4 per cent higher than the others. Average values for the blocks for each of the tests are shown in Figure 5. These results when plotted form a definite pattern related to the position on the side. It may be observed that

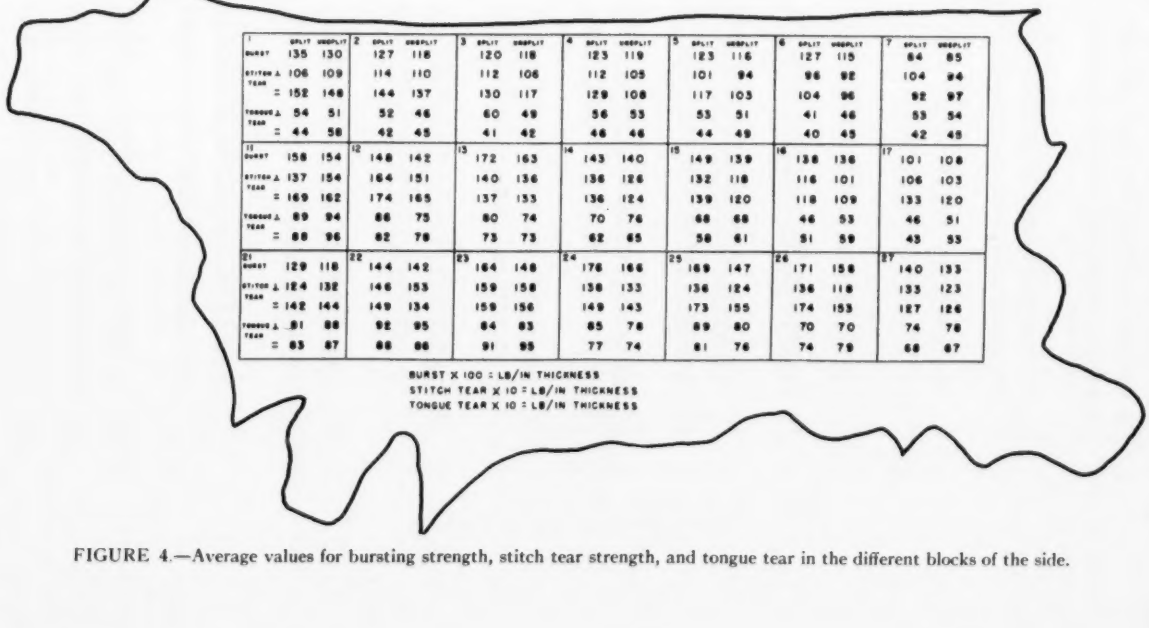


FIGURE 4.—Average values for bursting strength, stitch tear strength, and tongue tear in the different blocks of the side.

TABLE 2

Side Average for Split vs Unsplit Leather
Corresponding Sides

Hide	Tensile Strength				Stitch Tearing Strength				Tongue Tearing Strength				Burst Test		Grain Crack		Elongation at Break				Thickness	
	Perpendicular		Parallel		Perpendicular		Parallel		Perpendicular		Parallel						Perpendicular		Parallel			
No.	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit	Split	Unsplit
	10 lb/in²		10 lb/in²		10 lb/in Thk		10 lb/in Thk		10 lb/in Thk		10 lb/in Thk		100 lb/in Thk		Lb	Lb	%	%	%	%	Mils	Mils
A	449	415	528	474	133	118	155	137	67	63	63	66	136	142	993	979	68	68	60	53	98	112
B	391	431	464	508	126	121	146	139	69	76	64	69	143	139	521	891	61	63	55	56	90	113
C	432	421	573	564	140	118	131	130	68	62	63	59	143	131	658	977	65	64	53	52	92	112
D	459	430	525	502	130	126	144	133	72	63	65	63	155	117	431	534	62	64	53	53	87	106
E	389	412	475	498	130	117	146	136	74	71	70	70	143	127	610	813	59	60	49	50	91	119
F	435	454	544	587	120	124	133	141	72	68	63	66	147	137	478	831	63	65	52	49	93	118
G	430	432	581	588	121	115	145	136	70	66	68	63	157	129	850	1093	64	67	53	49	90	118
H	416	403	520	513	124	108	132	126	64	59	58	58	158	132	613	906	65	62	56	50	90	130
J	420	410	513	487	124	124	143	134	71	65	60	60	139	135	736	846	66	61	51	47	95	114
K	381	380	490	476	120	125	140	130	67	65	60	64	133	128	369	570	70	64	53	52	87	106
L	417	420	516	469	119	122	131	129	66	62	60	64	140	125	614	909	63	60	52	53	92	110
M	407	400	452	460	120	130	137	133	71	72	64	67	138	124	730	831	59	55	51	46	90	100
N	447	398	576	504	109	114	129	129	66	59	59	54	139	125	696	888	65	62	53	50	92	104
O	391	384	526	520	116	112	141	129	73	61	61	59	137	115	537	637	74	69	51	51	93	109
P	480	455	493	519	131	131	148	135	84	78	79	78	164	159	880	996	60	59	56	49	91	104
Q	398	420	475	483	137	127	149	126	72	75	68	74	145	138	610	842	61	69	51	55	84	98
R	472	471	506	548	140	131	149	133	67	77	67	75	154	153	999	1281	60	66	51	52	88	99
S	449	471	554	556	134	133	149	130	69	72	63	79	135	140	670	1110	66	64	56	55	88	112
T	435	434	478	494	129	120	146	133	72	70	66	67	139	143	660	1029	67	65	53	53	90	117
U	386	387	466	448	118	118	135	125	67	63	64	61	131	127	451	590	63	66	52	52	86	105
V	388	410	438	462	125	117	128	124	67	71	62	66	134	132	497	878	57	53	56	49	89	121
W	414	410	461	489	133	126	144	132	73	75	69	71	133	128	513	757	64	64	53	56	87	122
X	376	380	482	492	123	108	131	112	60	56	54	55	119	115	344	691	68	66	52	54	89	113
Y	463	452	553	564	130	121	151	141	73	72	69	73	141	156	935	1228	67	64	54	53	91	106
Z	344	398	420	473	110	110	116	116	53	58	50	59	113	122	464	769	68	65	58	55	89	117
XA	353	388	424	467	123	122	131	124	54	63	51	62	124	135	442	571	62	64	53	53	89	107
XB	400	407	522	520	136	122	146	135	65	67	61	65	122	122	367	618	71	69	55	53	92	111
XC	438	410	518	496	135	130	147	137	66	69	61	67	144	137	716	1039	62	64	54	56	90	105
XD	437	444	496	524	128	126	147	134	68	74	62	71	143	151	639	1107	67	65	55	50	93	116
XE	373	403	477	500	121	113	139	123	60	65	57	69	137	129	544	1002	67	66	55	57	96	130
Ave.	416	418	502	506	126	121	140	131	68	67	63	66	140	133	620	874	64	64	54	52	90	112

the blocks in the middle of each row, for example, 5, 15, and 25, give the lowest average percentage coefficients of variation for each of the tests, and that the blocks in the butt and shoulder areas give the highest coefficients. The coefficients of variation for all of the tests appear to follow the same pattern approximately.

TABLE 3

Correlation between Split and Unsplit Leathers for Tests from Block Averages and Side Averages

	Block Average Correlation Coefficient	Side Average Correlation Coefficient
Tensile strength (perpendicular)	0.86	0.74
(parallel)	0.89	0.72
Stitch tear (perpendicular)	0.92	0.54
(parallel)	0.95	0.66
Tongue tear (perpendicular)	0.94	0.59
(parallel)	0.97	0.65
Bursting strength	0.95	0.47
Elongation at break (perpendicular)	0.73	0.62
(parallel)	0.91	0.28

Coefficients of variation between side averages for tensile strength, stitch tear, tongue tear in two directions of test, and for burst test are given in Table 5. The coefficients of variation for the side averages are, of course, lower than those of the blocks, since the former are based on averages of 21 values. Stitch tear shows the lowest coefficient of variation, whereas tongue tear shows the highest percentage of variation. The values for all the tests as a whole show good uniformity.

b. Water Resistance Properties

Results of the water resistance properties for the split and the unsplit leathers are given in Figure 6 as averages for the blocks of the side. Each value given is the average of 14 to 16 individual measurements. These results give the water vapor permeability, the penetration point in seconds or the point at which the first drop of water penetrates the leather, and the amount of water absorbed by the wick. This test is made by placing a wick in the cup formed by the leather when placed in the machine and flexing it for 15 minutes. The amount of water absorbed by the leather is obtained also.

TABLE 4

Coefficient of Variation of Split and Unsplit Blocks Between Sides

	Tensile Strength					Stitch Tear Strength					Tongue Tear Strength					Bursting Strength		
	⊥		//			⊥		//			⊥		//					
Block	split	unsplit	split	unsplit	Ave.	split	unsplit	split	unsplit	Ave.	split	unsplit	split	unsplit	Ave.	split	unsplit	Ave.
	%	%	%	%		%	%	%	%		%	%	%	%		%	%	
1	22	17	18	16	18	19	24	19	15	19	19	20	18	27	21	16	13	14
2	20	10	24	22	19	16	16	17	12	15	24	14	30	19	22	23	22	22
3	18	13	17	13	15	13	13	10	12	12	14	13	15	16	14	14	17	16
4	15	9	13	13	12	13	9	11	10	11	17	11	12	16	14	15	12	14
5	12	13	11	9	11	14	11	14	11	12	13	12	15	14	14	12	11	12
6	17	15	15	14	15	13	12	11	10	12	13	14	16	14	14	18	12	15
7	16	12	20	18	16	15	10	15	11	13	22	18	17	16	18	16	16	16
11	15	14	32	26	22	17	14	13	13	14	18	19	17	21	19	16	15	16
12	11	9	15	19	14	16	12	16	12	14	14	18	20	19	18	14	12	13
13	14	16	11	13	14	12	14	8	12	12	21	21	18	15	19	13	14	14
14	11	11	17	11	12	12	18	10	10	12	15	23	14	13	16	15	16	16
15	10	9	15	10	11	11	9	10	10	10	14	13	12	11	12	13	14	14
16	14	15	20	12	15	12	14	10	9	11	17	16	13	14	15	13	16	14
17	16	14	17	13	15	14	12	16	18	15	12	14	17	14	14	16	25	20
21	17	24	29	32	26	17	16	22	20	19	20	21	24	22	22	14	17	16
22	20	17	17	18	18	14	16	19	22	18	20	15	18	17	18	18	10	14
23	9	12	23	31	19	11	15	12	11	12	15	13	15	17	15	17	16	16
24	10	10	12	12	11	11	11	21	9	13	17	10	13	11	13	14	17	16
25	10	13	14	8	11	14	10	12	17	13	11	11	12	12	12	8	9	8
26	14	19	33	39	26	11	23	13	20	17	13	17	14	12	14	15	12	14
27	19	13	22	20	18	15	14	18	18	16	18	13	14	13	14	13	8	10
Ave.	15	14	19	18	16	14	14	14	13	14	17	16	16	16	16	15	14	15

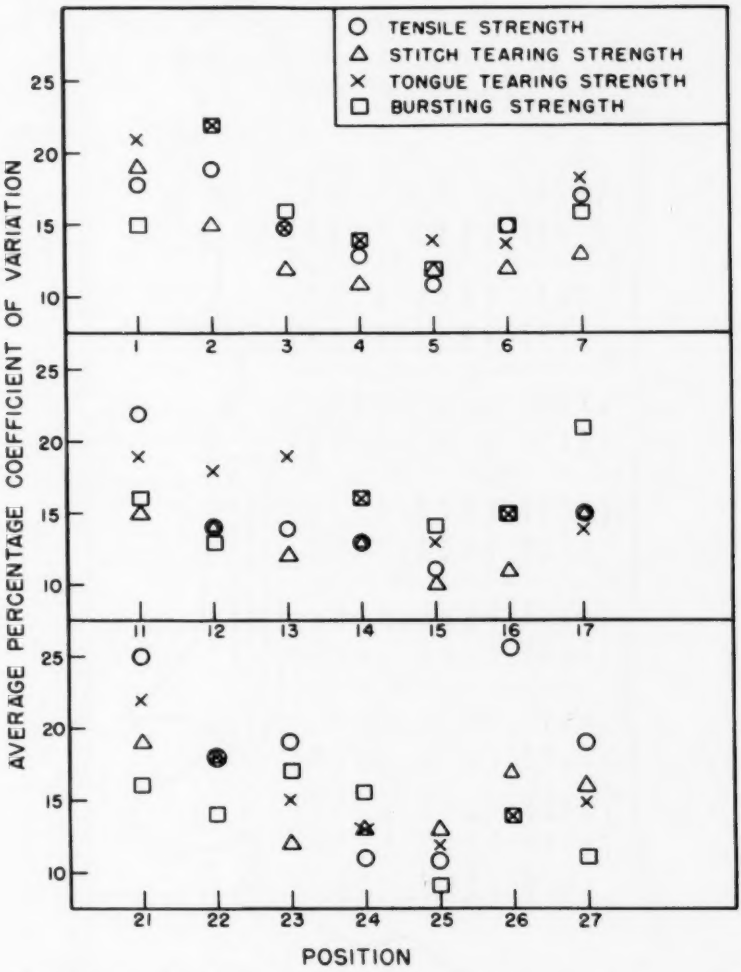
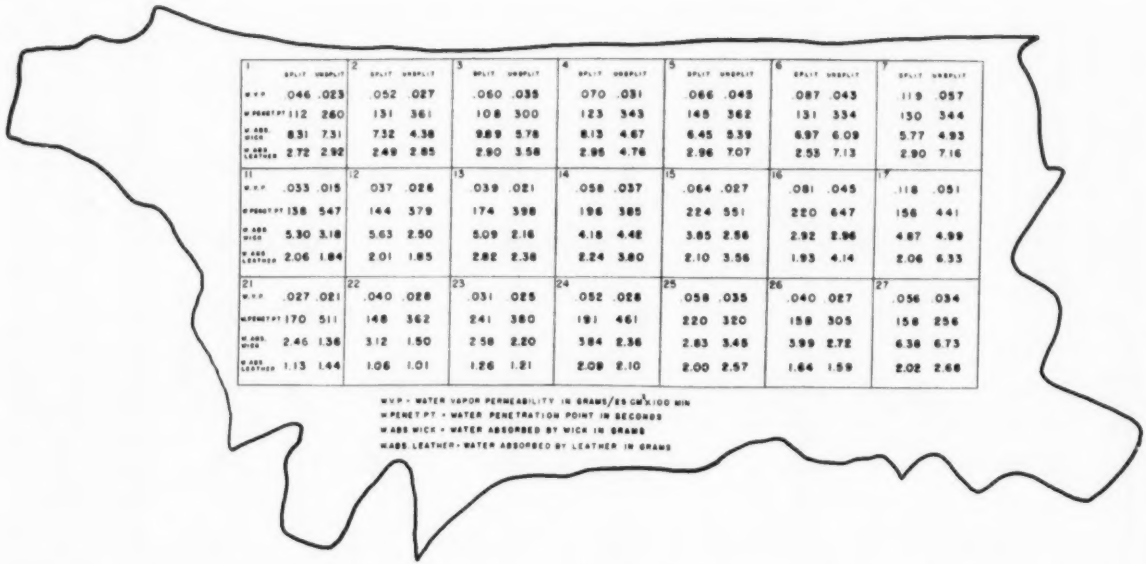


FIGURE 5.—Relation of the average percentage coefficient of variations for four physical tests with position on the side for split and unsplit chrome tanned leather.

Correlation coefficients for various water resistance relationships obtained in the same blocks of different sides are given in Table 6. Water vapor permeability shows a high negative correlation with grease content. A graph



	SPLIT	UNSPLIT
1		
W.V.P.	.046	.023
W.PENET.PT.	112	260
W.ABS. WICK	8.31	7.31
W.ABS. LEATHER	2.72	2.92
2		
W.V.P.	.052	.027
W.PENET.PT.	131	361
W.ABS. WICK	7.32	4.38
W.ABS. LEATHER	2.49	2.85
3		
W.V.P.	.060	.035
W.PENET.PT.	108	300
W.ABS. WICK	9.89	5.78
W.ABS. LEATHER	2.90	3.58
4		
W.V.P.	.070	.031
W.PENET.PT.	123	343
W.ABS. WICK	8.13	4.67
W.ABS. LEATHER	2.95	4.76
5		
W.V.P.	.066	.045
W.PENET.PT.	148	362
W.ABS. WICK	6.45	5.39
W.ABS. LEATHER	2.96	7.07
6		
W.V.P.	.087	.043
W.PENET.PT.	131	334
W.ABS. WICK	6.97	6.09
W.ABS. LEATHER	2.53	7.13
7		
W.V.P.	.119	.057
W.PENET.PT.	130	344
W.ABS. WICK	5.77	4.93
W.ABS. LEATHER	2.90	7.16
11		
W.V.P.	.033	.015
W.PENET.PT.	138	547
W.ABS. WICK	5.30	3.18
W.ABS. LEATHER	2.06	1.84
12		
W.V.P.	.037	.026
W.PENET.PT.	144	379
W.ABS. WICK	5.63	2.50
W.ABS. LEATHER	2.01	1.85
13		
W.V.P.	.039	.021
W.PENET.PT.	174	398
W.ABS. WICK	5.09	2.16
W.ABS. LEATHER	2.82	2.38
14		
W.V.P.	.058	.037
W.PENET.PT.	196	385
W.ABS. WICK	4.18	4.42
W.ABS. LEATHER	2.24	3.80
15		
W.V.P.	.064	.027
W.PENET.PT.	224	551
W.ABS. WICK	3.85	2.56
W.ABS. LEATHER	2.10	3.56
16		
W.V.P.	.081	.045
W.PENET.PT.	220	647
W.ABS. WICK	2.92	2.96
W.ABS. LEATHER	1.93	4.14
17		
W.V.P.	.118	.051
W.PENET.PT.	156	441
W.ABS. WICK	4.87	4.99
W.ABS. LEATHER	2.06	6.33
21		
W.V.P.	.027	.021
W.PENET.PT.	170	511
W.ABS. WICK	2.46	1.36
W.ABS. LEATHER	1.13	1.44
22		
W.V.P.	.040	.028
W.PENET.PT.	148	362
W.ABS. WICK	3.12	1.50
W.ABS. LEATHER	1.06	1.01
23		
W.V.P.	.031	.025
W.PENET.PT.	241	380
W.ABS. WICK	2.58	2.20
W.ABS. LEATHER	1.26	1.21
24		
W.V.P.	.052	.028
W.PENET.PT.	191	461
W.ABS. WICK	3.84	2.36
W.ABS. LEATHER	2.08	2.10
25		
W.V.P.	.058	.035
W.PENET.PT.	220	320
W.ABS. WICK	2.83	3.45
W.ABS. LEATHER	2.00	2.57
26		
W.V.P.	.040	.027
W.PENET.PT.	158	305
W.ABS. WICK	3.99	2.72
W.ABS. LEATHER	1.64	1.59
27		
W.V.P.	.056	.034
W.PENET.PT.	158	256
W.ABS. WICK	6.38	6.73
W.ABS. LEATHER	2.02	2.68

W.V.P. = WATER VAPOR PERMEABILITY IN GRAMS/25 CM²X100 MIN
W.PENET.PT. = WATER PENETRATION POINT IN SECONDS
W.ABS WICK = WATER ABSORBED BY WICK IN GRAMS
W.ABS LEATHER = WATER ABSORBED BY LEATHER IN GRAMS

FIGURE 6.—Average values for water vapor permeability, water penetration point, water absorption by the wick, and water absorption by the leather for the different blocks of the sides.

TABLE 5

Coefficients of Variation Between Side Averages for the Physical Tests

Leather	Tensile Strength		Stitch Tear Strength		Tongue Tear Strength		Bursting Strength
	$\frac{\perp}{\sigma}$ %	$\frac{/\!/}{\sigma}$ %	$\frac{\perp}{\sigma}$ %	$\frac{/\!/}{\sigma}$ %	$\frac{\perp}{\sigma}$ %	$\frac{/\!/}{\sigma}$ %	$\frac{}{\sigma}$ %
Split	8.3	8.6	6.6	5.6	9.1	9.2	8.1
Unsplit	6.1	7.4	5.7	5.0	9.1	9.7	8.6

TABLE 6

Correlation Coefficients for Various Water Resistance Relationships

	Split	Unsplit
Water vapor permeability versus grease contents	−0.78	−0.81
Penetration time vs wick pickup	−0.81	−0.56
Pickup in leather vs wick pickup	0.78	0.60
Wick pickup vs grease content	−0.35	−0.46
Leather pickup vs grease content	−0.23	−0.65

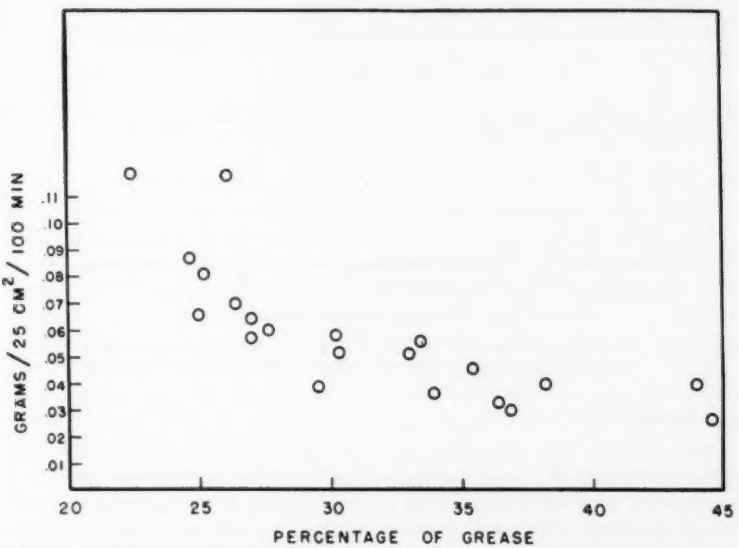


FIGURE 7.—Variation of water vapor permeability with grease content for split and unsplit chrome-tanned leathers.

showing the decrease in water vapor permeability with increase in grease content for split leather is shown in Figure 7. Split leather shows a high correlation between time of penetration and wick pickup. This graph is shown in Figure 8. The unsplit leather shows a significant correlation between water pickup by leather and grease content. These results are plotted in Figure 9. An additional factor which influences the comparative results between split and unsplit leather is the thickness. Figure 6 indicates that the water vapor permeability of the thicker unsplit leather is lower than that of the split leather. (Refer to Figure 3 for thickness values.) One other factor that may influence the comparative results between split and unsplit leather is that the grease may be distributed more uniformly in the former than in the latter.

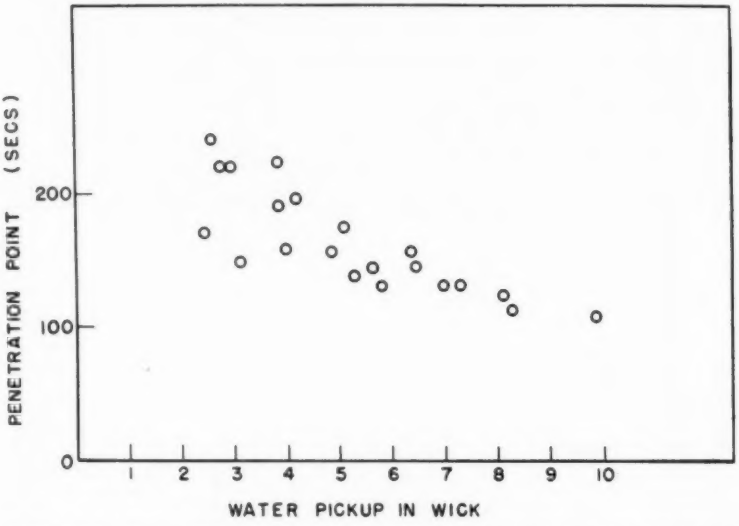


FIGURE 8.—Comparison of water pickup in wick with penetration point in the Maeser tests for water penetration of split and unsplit chrome-tanned leathers.

c. Chemical Tests

The results of the chemical tests on the split and the unsplit leathers are given as averages of the various blocks of a side in Figure 10. These results are averages of 14 or of 16 individual sides in the lot. Back and butt locations which constitute the denser portions of the side have high hide substance concentrations and low grease contents. It may be observed that the grease content is 100 per cent greater in block 21 than in block 7. This is the greatest

variation between blocks of the side and is indicative of the fiber density in the two locations.

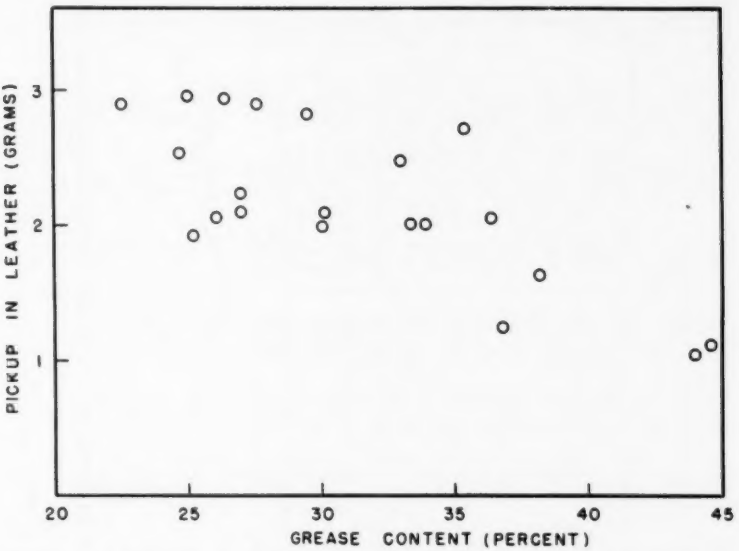


FIGURE 9.—Comparison of pickup of water in leather with grease content in the Maeser test for water penetration of split and unsplit chrome-tanned leathers.

The results of the chemical tests and calculations made from these are given in Tables 7 and 8. Calculations shown in these tables and Figure 11 indicate that the moisture and the chrome content are directly proportional to the hide substance. The ratio of moisture to hide substance in all blocks is approximately 0.2, whereas that of the chromic oxide to hide substance is approximately .065 in all blocks. Figure 11 indicates that the grease content is inversely related to the hide substance content. This ratio is, however, not constant for the product of hide substance and grease given in Tables 7 and 8, but decreases with increase in hide substance content. Therefore, grease content, chromic oxide content, and moisture content all bear some relation to the hide substance content.

Tables 7 and 8 also give the total composition of the split and unsplit chrome-tanned leathers. This is obtained by adding the percentages of all of the constituents calculated on the moisture free basis. Since ashing the leather reduces the chromium tanning salt to Cr_2O_3, the value for the latter was multiplied by the factor 2.73 to convert it back to chrome tanning sub-

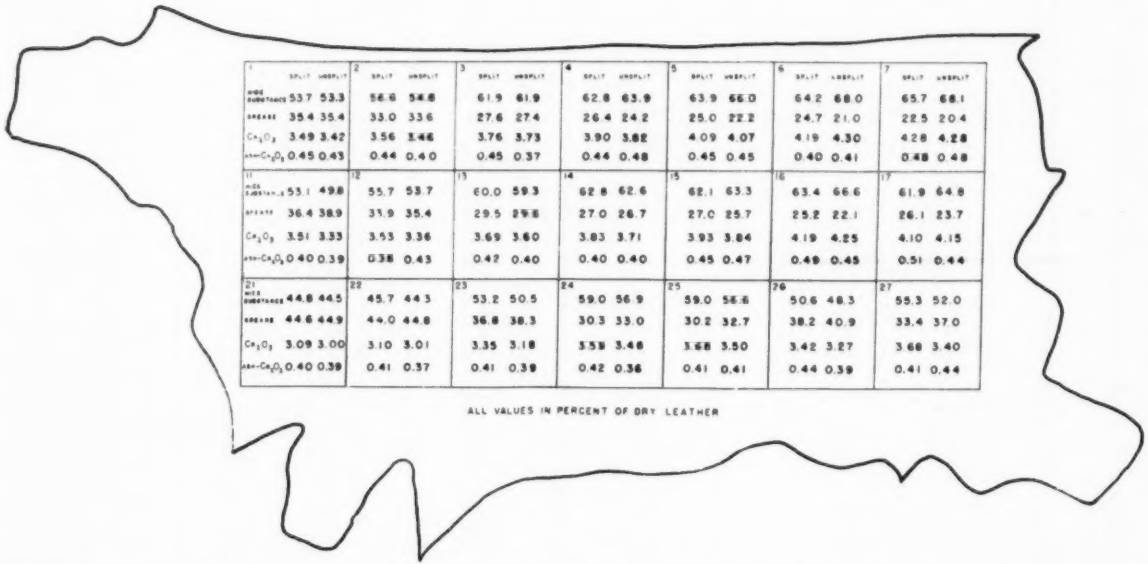


FIGURE 10.—Average values for the chemical constituents in the different blocks of the sides of split and unsplit chrome-tanned leather.

TABLE 7

Chemical Analysis (Split Leather)

PART I

Block	1	2	3	4	5	6	7	11	12	13	14
Hide substance, %	53.7	56.6	61.9	62.8	63.9	64.2	65.7	53.1	55.7	60.0	62.8
Chromic oxide, Cr_2O_3, %	3.49	3.56	3.76	3.90	4.09	4.19	4.28	3.51	3.53	3.69	3.83
Ash, %	3.94	4.00	4.21	4.34	4.54	4.59	4.76	3.91	3.91	4.11	4.23
Grease, %	35.4	33.0	27.6	26.4	25.0	24.7	22.5	36.4	33.9	29.5	27.0
Moisture, %	11.0	11.4	12.6	12.7	13.1	12.8	13.1	10.8	11.5	12.2	13.0
pH	3.3	3.3	3.2	3.2	3.3	3.3	3.4	3.3	3.3	3.2	3.2
Moisture / Hide Substance	0.205	0.201	0.204	0.202	0.205	0.199	0.199	0.203	0.206	0.203	0.207
Cr_2O_3 / Hide substance	0.065	0.063	0.061	0.062	0.064	0.065	0.065	0.066	0.063	0.062	0.061
Ash—Cr_2O_3, %	0.45	0.44	0.45	0.44	0.45	0.40	0.48	0.40	0.38	0.42	0.40
2.73 x Cr_2O_3, %	9.53	9.72	10.26	10.65	11.17	11.44	11.68	9.58	9.64	10.07	10.46
Hide substance x grease	0.190	0.187	0.171	0.166	0.160	0.159	0.148	0.193	0.189	0.177	0.170
Total Composition											
Hide substance, %	53.7	56.6	61.9	62.8	63.9	64.2	65.7	53.1	55.7	60.0	62.8
Grease, %	35.4	33.0	27.6	26.4	25.0	24.7	22.5	36.4	33.9	29.5	27.0
2.73 x Cr_2O_3, %	9.53	9.72	10.26	10.65	11.17	11.44	11.68	9.58	9.64	10.07	10.46
Ash—Cr_2O_3, %	0.45	0.44	0.45	0.44	0.45	0.40	0.48	0.40	0.38	0.42	0.40
Analysis sum, %	99.08	99.76	100.21	100.29	100.52	100.74	100.36	99.48	99.62	99.99	100.66

PART II

Block	15	16	17	21	22	23	24	25	26	27
Hide substance, %	62.1	63.4	61.9	44.8	45.7	53.2	59.0	59.0	50.6	55.3
Chromic oxide, Cr_2O_3, %	3.93	4.19	4.10	3.09	3.10	3.35	3.59	3.68	3.42	3.68
Ash, %	4.38	4.68	4.61	3.49	3.51	3.76	4.01	4.09	3.86	4.09
Grease, %	27.0	25.2	26.1	44.6	44.0	36.8	30.3	30.2	38.2	33.4
Moisture, %	12.7	13.1	12.5	9.3	9.4	11.1	11.9	12.2	10.2	11.2
pH	3.2	3.3	3.3	3.5	3.5	3.3	3.2	3.3	3.3	3.3
Moisture / Hide substance	0.205	0.207	0.202	0.208	0.206	0.209	0.202	0.207	0.202	0.203
Cr_2O_3 / Hide substance	0.063	0.066	0.066	0.069	0.068	0.063	0.061	0.062	0.068	0.067
Ash—Cr_2O_3, %	0.45	0.49	0.51	0.40	0.41	0.41	0.42	0.41	0.44	0.41
2.73 x Cr_2O_3, %	10.73	11.44	11.19	8.44	8.46	9.15	9.80	10.05	9.34	10.05
Hide substance x grease	0.168	0.160	0.162	0.200	0.201	0.196	0.179	0.178	0.193	0.185
Total Composition										
Hide substance, %	62.1	63.4	61.9	44.8	45.7	53.2	59.0	59.0	50.6	55.3
Grease, %	27.0	25.2	26.1	44.6	44.0	36.8	30.3	30.2	38.2	33.4
2.73 x Cr_2O_3, %	10.73	11.44	11.19	8.44	8.46	9.15	9.80	10.05	9.34	10.05
Ash—Cr_2O_3, %	0.45	0.49	0.51	0.40	0.41	0.41	0.42	0.41	0.44	0.41
Analysis sum, %	100.28	100.53	99.70	98.24	98.57	99.56	99.52	99.66	98.58	99.16

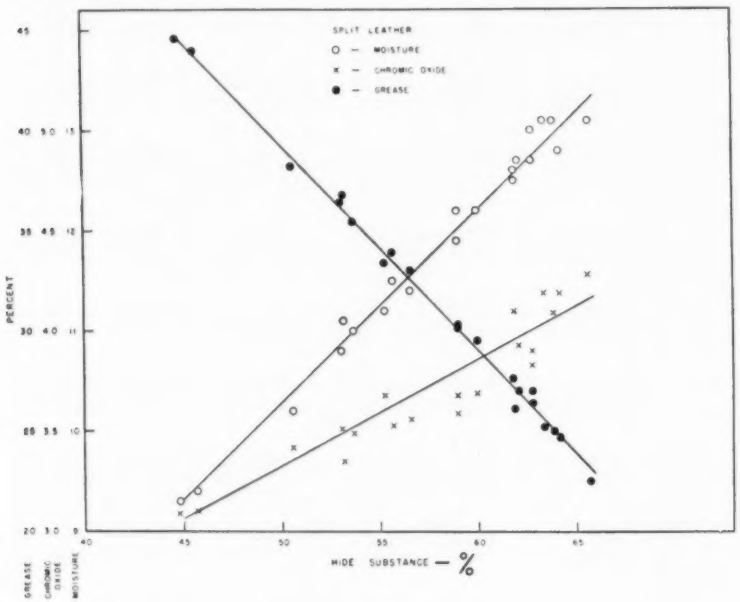


FIGURE 11.—Relation of moisture, chrome oxide, and grease content with hide substance for split chrome-tanned leather.

stance. This factor is suggested by V. Kubelka [6]. It may be observed that when the Cr_2O_3 content is subtracted from the ash a fairly constant value of about 0.4 is obtained for all of the blocks. This is apparently the amount of inorganic salt which is in the leather. The sum of the values for hide substance, grease, Cr_2O_3 x 2.73, and the ash – Cr_2O_3 should make up the total composition of chrome-tanned leather. It may be observed that these sums for all blocks for the split and the unsplit leathers range from 97.69 to 101.15 per cent. It is interesting to note that those locations giving the lower sums have the highest grease contents and those giving the higher sums have the lowest grease contents. This may be explained from the results of Dahl [7] who found that the precision in the method used for the determination of nitrogen was lowered by high grease contents.

The percentage coefficient of variation of hide substance, grease, and chromic oxide for the blocks between sides is given in Table 9. The percentage variation of these constituents between side averages is given in Table 10. In several cases the variation between blocks is less than that between side averages, which probably indicates that since the variability

TABLE 8

Chemical Analysis (Unsplit Leather)

PART I

Block	1	2	3	4	5	6	7	11	12	13	14
Hide substance	53.3	54.8	61.9	63.9	66.0	68.0	68.1	49.8	53.7	59.3	62.6
Chromic oxide, Cr_2O_3, %	3.42	3.46	3.73	3.82	4.07	43.0	4.28	3.33	3.36	3.60	3.71
Ash, %	3.85	3.86	4.10	4.30	4.52	4.71	4.76	3.72	3.79	4.00	4.11
Grease, %	35.4	33.6	27.4	24.2	22.2	21.0	20.4	38.9	35.4	29.6	26.7
Moisture, %	11.0	11.5	12.7	13.4	13.7	14.0	14.0	10.6	11.2	12.3	12.7
pH	3.1	3.2	3.1	3.1	3.0	3.0	3.0	3.2	3.2	3.1	3.0
Moisture / Hide substance	0.206	0.210	0.205	0.210	0.208	0.206	0.206	0.213	0.209	0.207	0.203
Cr_2O_3 / Hide substance	0.064	0.063	0.060	0.060	0.062	0.063	0.063	0.067	0.063	0.061	0.059
Ash—Cr_2O_3, %	0.43	0.40	0.37	0.48	0.45	0.41	0.48	0.39	0.43	0.40	0.40
2.73 x Cr_2O_3, %	9.34	9.45	10.18	10.43	11.11	11.74	11.68	9.09	9.17	9.83	10.13
Hide substance x grease	0.189	0.184	0.170	0.155	0.147	0.143	0.139	0.194	0.190	0.176	0.167
Total Composition											
Hide substance, %	53.3	54.8	61.9	63.9	66.0	68.0	68.1	49.8	53.7	59.3	62.6
Grease, %	35.4	33.6	27.4	24.2	22.2	21.0	20.4	38.9	35.4	29.6	26.7
2.73 x Cr_2O_3, %	9.34	9.45	10.18	10.43	11.11	11.74	11.68	9.09	9.17	9.83	10.13
Ash—Cr_2O_3, %	0.43	0.40	0.37	0.48	0.45	0.41	0.48	0.39	0.43	0.40	0.40
Analysis sum, %	98.47	98.25	99.85	99.01	99.76	101.15	100.66	98.18	98.70	99.13	99.83

PART II

Block	15	16	17	21	22	23	24	25	26	27
Hide substance, %	63.3	66.6	64.8	44.5	44.3	50.5	56.9	56.6	48.3	52.0
Chromic Oxide, Cr_2O_3, %	3.84	4.25	4.15	3.00	3.01	3.18	3.48	3.50	3.27	3.40
Ash, %	4.31	4.70	4.59	3.39	3.38	3.57	3.84	3.91	3.66	3.84
Grease, %	25.7	22.1	23.7	44.9	44.8	38.3	33.0	32.7	40.9	37.0
Moisture, %	12.9	13.5	13.1	9.1	9.2	10.4	11.5	11.5	9.7	10.4
pH	3.0	3.0	3.1	3.3	3.3	3.2	3.1	3.1	3.2	3.2
Moisture / Hide substance	0.204	0.203	0.202	0.204	0.208	0.206	0.202	0.203	0.201	0.200
Cr_2O_3— / Hide substance	0.061	0.064	0.064	0.067	0.068	0.063	0.061	0.062	0.068	0.065
Ash—Cr_2O_3, %	0.47	0.45	0.44	0.39	0.37	0.39	0.36	0.41	0.39	0.44
2.73 x Cr_2O_3, %	10.48	11.60	11.33	9.19	8.22	8.68	9.50	9.56	8.93	9.28
Hide substance x grease	0.163	0.147	0.154	0.200	0.198	0.193	0.188	0.185	0.198	0.192
Total Composition										
Hide substance, %	63.3	66.6	64.8	44.5	44.3	50.5	56.9	56.6	48.3	52.0
Grease, %	25.7	22.1	23.7	44.9	44.8	38.3	33.0	32.7	40.9	37.0
2.73 x Cr_2O_3, %	10.48	11.60	11.33	8.19	8.22	8.68	9.50	9.56	8.93	9.28
Ash—Cr_2O_3, %	0.47	0.45	0.44	0.39	0.37	0.39	0.36	0.41	0.39	0.44
Analysis sum, %	99.95	100.75	100.27	97.98	97.69	97.87	99.76	99.27	98.52	98.72

between locations is so low the results are influenced not only by position variations but by the precision of the test method. Thus these two variations are considered to be due to chance. Results for both the split and unsplit leathers show good agreement.

TABLE 9

Percentage Coefficient of Variation for Blocks Between Sides for Chemical Constituents

Block	Hide Substance		Grease		Chrome oxide	
	split %	unsplit %	split %	unsplit %	split %	unsplit %
1	3.5	5.0	6.5	7.3	4.0	4.0
2	5.6	4.2	8.2	5.1	4.2	2.9
3	3.5	3.2	8.7	9.5	4.0	5.1
4	3.8	3.8	8.0	9.5	5.1	4.2
5	3.0	3.9	8.8	10.4	3.9	4.9
6	3.8	1.9	9.7	6.2	5.0	4.0
7	3.2	3.5	12.0	12.2	4.4	5.6
11	7.7	4.8	11.3	5.4	6.6	3.3
12	4.3	5.0	7.7	11.6	3.4	5.4
13	3.7	4.7	8.5	8.4	5.7	3.6
14	7.3	3.6	5.2	8.2	3.4	3.8
15	2.7	3.2	6.7	7.8	3.6	3.4
16	2.8	3.6	8.7	9.0	4.1	4.9
17	2.4	2.8	6.5	10.1	4.6	5.3
21	11.2	8.8	7.4	7.8	3.2	5.3
22	5.5	7.0	6.4	6.7	5.2	6.6
23	5.1	7.5	7.6	10.2	3.9	8.8
24	4.2	4.0	8.2	7.9	3.6	3.7
25	5.7	3.9	9.3	9.8	4.1	4.8
26	6.7	8.3	10.5	9.8	6.4	8.2
27	7.1	6.9	7.5	12.2	3.8	6.2

TABLE 10

Percentage Coefficient of Variation for Side Averages for Chemical Constituents
(Based on split leather)

	Coefficient of Variation	
	Split	Unsplit
	%	%
Hide substance	3.0	3.4
Grease	6.2	6.8
Chromic oxide	3.7	3.8

V. Summary

Results have been obtained for the physical and chemical tests on chrome-tanned leathers for split and unsplit sides taken from the same hides. The splitting down to approximately 6 ounces, which is the thickness for retanned upper leathers, did not alter appreciably the strength properties of the leather.

Correlation coefficients for the physical tests between split and unsplit side averages for the same hide were good, and the correlation coefficient of the results between blocks was excellent for most of the tests. Results of the chemical tests showed excellent agreement in all respects between the two sets of sides.

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The Iso-electric Points of Chromium Collagen Compounds

By K. H. Gustavson

The hydrogen ion activity (or pH value) at which an ampholyte is electrically neutral is called the iso-electric point. The sum of the ionized fractions of the basic groups equals then the sum of the ionized fractions of the acid groups. Further, it follows that the iso-electric point of a protein is that pH value at which it does not migrate in an electric field. Chemical treatments which affect the ionic protein groups of the protein will alter the iso-electric point. It is also evident that by the study of the reactivity of collagen for cationic and anionic agents this important characteristic of proteins can be determined. Hence the shift of the iso-electric point which may result from irreversible fixation of tanning agents will indicate the type of protein groups involved in the particular reaction and be of value for the formulation of theoretical concepts of the tanning mechanism.

Thomas and Kelly [1] used acid and basic dyestuffs for determination of the iso-electric point of collagen (hide powder) by a technique based upon principles

developed by Loeb in his researches on gelatin [2]. They found hide powder iso-electric at pH 5.0. The same technique was applied by the author [3, 4] for determination of the iso-electric point of hide powder and pelt tanned by means of formaldehyde, various vegetable tannins, sulfo-acid syntans and cationic and anionic chromium salts. The results of these unpublished investigations from 1924–26 are included in Wilson's monograph [5] (personal communications) and have been cited in the literature [6].

It was found that by tanning hide powder and pelt by means of formaldehyde, sulfo-acids and vegetable tannins the iso-electric point of the protein was shifted toward the acid side, or from pH 5.5 to a pH in the vicinity of 4. These findings have been confirmed through other methods (see, e. g.,([8])). Interaction with and inactivation of cationic protein groups take place in the tannages mentioned. As to the effect of chromium salts on the iso-electric function of collagen, the findings are contradictory and the whole problem is in an unsatisfactory state. It was found in the early work that collagen tanned by means of basic chromic sulfate (cationic chromium complexes) was iso-electric in the pH range 6.5–7; indicating the preferential inactivation of acidic protein groups. In tanning hide powder by means of anionic chromium complexes, as oxalato-chromiate of pH 5.0, the iso-electric point of the hide powder was lowered from pH 5.5 to pH 3.8–4.5, the average being 4.2; which alteration was taken as an evidence for the inactivation of the basic protein groups by this agent [5]. In a following communication [4], the effect of the two types of chromium compounds upon collagen in regards to its fixation of acid and basic dyestuffs was investigated. It was found that the acid (anionic) dyestuffs possessed a very much lower affinity for collagen tanned by means of anionic chromium complexes than for the stock of cationic chrome tannage. On the other hand, the degree of affinity of the two types of chromed collagen was reversed in their behavior towards basic (cationic) dyestuffs. Thus, citing some figures, methylene blue, buffered at pH 7.4 was 95–100 per cent exhausted by hide powder of anionic chrome tannage whereas the specimens tanned by means of cationic basic chromic sulfates only fixed 30–40 per cent of the quantity of basic dyestuff given. The data indicated the iso-electric point of the anionic tanned collagen to be in the vicinity of pH 4. The corresponding values of collagen tanned by cationic chromium salts were located to the pH range >6.

In an electrophoretic investigation of hide powder treated in solutions of basic chromic sulfate (cationic chromium complexes), on one hand, and in solutions of the chromic sulfate containing salts of complex-forming organic acids (partly anionic chromium), on the other hand, Theis [7] found that tanning by means of simple basic sulfate of chromium (cationic) produced a shift of the iso-electric point of collagen toward the acid side, or from pH 5.5 to pH 4.5. Accordingly, the cationic chrome fixation was indicated to involve the basic protein groups chiefly. By masking the chromic sulfate,

yielding partially anionic complexes, Theis found the iso-electric point of the tanned hide powder at a higher pH range than that of the untreated hide powder; such high pH values as 6.6 being recorded. The tendency of the shift of the iso-electric point due to the fixation of the two types of chrome tanning agents by collagen found by Theis is hence contrary to the figures obtained by means of the dyestuff technique.

Since this problem is of paramount importance for the theoretical fundamentals of the chrome tanning process and further, since Theis' finding seemed irreconcilable with the experimental facts from other sources, documented in the literature by numerous investigators, studies of the electrophoretic behavior of chrome collagen were commenced in 1942 under the guidance of experts on electrophoresis of proteins at the Institute of Physical Chemistry, the University of Upsala. In view of a more recent contribution to this problem [8] and considering the finding that Theis' data are invalidated by grave experimental oversight, the publication of the results from this re-investigation was prompted, particularly since recently published investigations of Otto [9] substantiate the older findings. The present findings show that Theis' results are vitiated by his unsuitable choice of buffers, *i. e.*, compounds containing anions of high complex forming power for chromium (acetate and phosphate), which tend to reverse the electric charge of the chromium complexes fixed by collagen. This will be demonstrated in the experimental part. Further, Theis *dried* his chromed hide powders before carrying out the determinations. However, by drying of chrome leather its electrochemical behavior is radically changed [9, 10].

Recently, Cassel and Kanagy [8] have published a scholarly investigation on the electrophoretic behavior of native collagen (unlimed) and modified collagens, including specimens tanned by means of basic chromic sulfate (cationic). However, their work also is marred by the choice of buffers unsuitable for investigating chrome leather. They find that by incorporation of small amounts of chromium into the collagen structure (1 per cent Cr_2O_3), its iso-electric point is shifted markedly toward the acid side, or from pH 7 to pH 4. By increasing the amount of fixed chromium, the peculiar finding of an increase of the pH of the iso-electric point was recorded; the iso-electric state being reached at pH 5 for the specimen containing 2.5 per cent fixed Cr_2O_3. Already at this point, it is advisable for didactic reasons to examine the figures given from the point of view of complex chemistry. Theis employed chromed hide powder which had been *dried* before carrying out the determination. Even by careful airdrying of chrome leather, the state of the complexes introduced into the chrome leather in the cationic form is altered, the tendency being to shift the iso-electric point of the original *moist* leather toward the acid side as demonstrated independently by Otto [9] and the present author [10]. This displacement is of the order of two pH-units in some instance [9]. Since, the *original* state of the chromium complexes in their direct combination

with hide protein is the paramount issue for the theory of the chrome tanning mechanism, the data from experiments with dried chromed hide powder have no bearing on the problem under discussion. Regarding the action of the buffers, it is to be noted that Theis kept his chromed specimens in the solutions of complex-forming buffers for 40 hours before the electrophoretic examination, allowing ample time for changes to take place in the chromium complexes. Further, no attention was paid to the presence of protein-bound acid in the chromed hide powder. This acid should be removed during the preparation of the stock for electrophoresis by the neutralization-diffusion method [11] or by treating the stock for 3–4 hours in a 4 per cent aqueous solution of pyridine [12]. This will facilitate keeping the pH constant, difficult with buffers of low capacity in the pH range employed such as the borate system.

Examining the data given by Cassel and Kanagy for the specimen tanned by means of cationic chromium complexes, the large displacement of the pH value of the iso-electric point found at low content of fixed chromium is likely the result of the mass action effect of the acetate and phosphate ions of the buffers on the small amount of chromium of the tanned hide powder. The same solutions should be less effective on chromed hide powder of higher chromium content since the ratio of the amount of complex-forming anions of the solution to the amount of chromium is lowered. Further, the degree of chrome tannage employed is far below the standard of regular chrome tanned leather. However, any further discussion of the data of Cassel and Kanagy is of questionable value, since it is not known (but probable) that even by the mild form of dehydration practised by these authors changes in the chromium complexes have been induced in the stock already at this stage of the method, invalidating any conclusion regarding the original chrome fixation. It should be noted that in the old investigations by means of the dyestuff technique [4, 5] as well as in the series reported in the present paper, the tanned collagen had not been dried at any stage of the process.

Material

Collagen of cationic chrome tannage. Freiberg hide powder, passing 20 mesh sieve, and neutral calf skin pelt (=10 g. collagen in 200 ml. solution) were tanned for 2 hours and 96 hours in a 66 per cent acid chrome sulfate liquor ($Cr_2(OH)_2(SO_4)_2.Na_2SO_4$) containing 15.0 g/l. Cr_2O_3. At this concentration of the aged solution 96 per cent of the total chromium was present in the cationic form [13]. Also hide powder coarser than 10 mesh was tanned in the same manner for use in the special technique of Professor S. M. Neale. After completed tanning the stock was washed free from uncombined matter of the tan bath. Half of the stock was treated in 250 ml. water under intermittent shaking for 48 hours, the acid diffusing out being gradually neutralized by alkali (diffusion-neutralization method [11]). The other half of the stock

was shaken for 4 hours in 100 ml. of 4 per cent aqueous solution of pyridine [12] and washed thoroughly for several weeks. It is not advisable to apply electro-dialysis for removal of the protein-bound acid, since it is difficult to keep the sulfato groups intact by this method. Part of the strongly chrome tanned specimen of pelt was dehydrated with acetone.

Collagen of anionic chrome tannage. Hide powder, in portions of 5 g. was treated in 200 ml. solutions of sodium diol-tetra-oxalato-chromiate [14], containing 20.0 g/l. Cr_2O_3 at pH 5.0 for 48 hours and 14 days. The stock was freed from uncombined matter by washing. The samples were kept several months in water, frequently changed, before the tests were carried out. The pertinent data of the composition of the chromed collagen preparations are given in Table I.

TABLE I

Analysis of chromed specimens

No.	Substrate	Type of chromium salt	% Cr_2O_3 on collagen basis	% acidity of the chromium complex
1.	Hide powder	Cationic	5.2	32
2.	" "	"	10.6	33
3.	Pelt	"	5.1	33
4.	"	"	10.3	35
5.	Hide powder	Anionic	3.7	—
6.	" "	"	8.9	—
7.	Coarse hide powder	Cationic	4.8	33
8.	" " "	Anionic	3.6	—

The average composition of the sulfato-chromium-complexes fixed by collagen corresponds to the empirical formula ($Cr_2.OSO_4$).

Experimental

Buffers. The buffers used in the electrophoresis experiments were boric acid – borate in 0.02 *N* potassium chloride. In some comparative experiments aimed at an experimental test of the view of the source of error in the electrophoresis data discussed being the complex forming buffers used, a solution of an acetate buffer was employed (0.02 *N* potassium chloride + 0.02 *N* sodium acetate + needed acetic acid).

Electrophoresis. By grinding of the tanned hide powder in the wet state and by treatment in a special ball mill, it was not possible to prepare a suspension of a degree of stability required for the electrophoresis in the Tiselius apparatus (experiments by Dr. H. Svensson of Institute of Physical Chemistry of the University of Upsala). For the micro-electrophoresis method, the

degree of pulverization of the decanted suspensions (2-6 μ of the majority of particles) was satisfactory. By grinding of the chrome tanned hide powder by hand with the buffer solution in an agate mortar, a suitable suspension was obtained. The suspensions were then dialized against the buffer solutions for a few hours. A modified apparatus of the horizontal micro-electrophoresis type of cell, described by Abramson, Moyer and Gorin [15], constructed and operated by B. Olofsson of the Swedish Textile Research Institute, Gothenburg, was employed. The cell had the dimensions: 55 x 20 x 9 mm and was mounted on a microscope. The mobility of the suspended particles was measured by an ocularmicrometer and figured as μ /sec/volt/cm. The electrode system was: silver-silver chloride-saturated potassium chloride solution. In the pH range 4–6, the values of the mobility form almost a straight line for each series. A marked spreading of values was found at pH values far from the iso-electric range.

Electrokinetic method of S. M. Neale. This method is based upon the production of an electric current by forcing a stream of a dilute solution of an electrolyte (potassium chloride) through a plug of fibers (hide powder in the tanned or untreated states) in a tube. The surface potential of the fibers is measured. The coarse hide powder was used for these measurements. The reversible electrodes (silver-silver chloride) are in direct contact with the plug. The surface potential is given in millivolts. For further details reference is given to the original papers of Neale and his collaborators [16]. Professor Neale was kind enough to determine the surface potential of samples of chromed hide powder and chromed pelt from which an idea of the location of the iso-electric points can be gained.

Dyestuff technique. Regular hide powder of the same tannage as described was used for these series. It was freed from protein-bound acid by the diffusion-neutralization method. Portions equal to 0.5 g. collagen were treated 24 hours in 50 ml. buffer solutions (borate) of pH 3.6 to 8.0, with 0.2 pH intervals. The buffer solution was removed by filtering through a glass-filter and the dyestuff added in 50 ml. of the corresponding buffer solution to an amount equal to 10 per cent of the weight of the stock. The dyestuffs employed were: Acid fuchsine, methanile yellow, methylene blue and methyl violet. After shaking the specimens for 2 hours, the solution was removed by suction and the stock washed with the corresponding buffer solution and finally with water on the glass filter in order to remove unfixed dyestuff. The pH value at which a distinct staining of the hide powder was obtained, was taken as the iso-electric point.

Results

Electrophoresis. The main results are given in Fig. 1 by using boric acid-borate-potassium chloride buffers which do not interact with the chromium complexes in the dilution employed, the following pH values corresponding

to the iso-electric point were obtained. For the cationic chromed hide powder (no. 1) pH 6.4; for the anionic chromed hide powder (no. 5) pH 4.8 and for no. 4 of the same tannage pH 4.4. Untreated hide powder used as a blank was iso-electric at pH 5.4. By using the acetate buffer hide powder no. 1 of cationic tannage was iso-electric at pH 4.2. For the anionic chromed stock no. 5, this buffer gave identical iso-electric point to that of the borate-buffered specimen. Accordingly, by employing an acetate buffer the hide powder tanned by means of cationic chromium complexes behaves like anionic chromed collagen, probably as a result of the penetration of acetate anions into the chromium complex making it into an anionic complex, subsequently interacting with the basic protein groups. Since the oxalate group is firmly held and possesses greater complex-forming power for chromium than the acetate groups, the anion of the buffer has no effect on the fixed oxalato-chromiate complex and on its valency partition on collagen. This finding will explain the peculiar results obtained by Theis and by Cassel and Kanagy

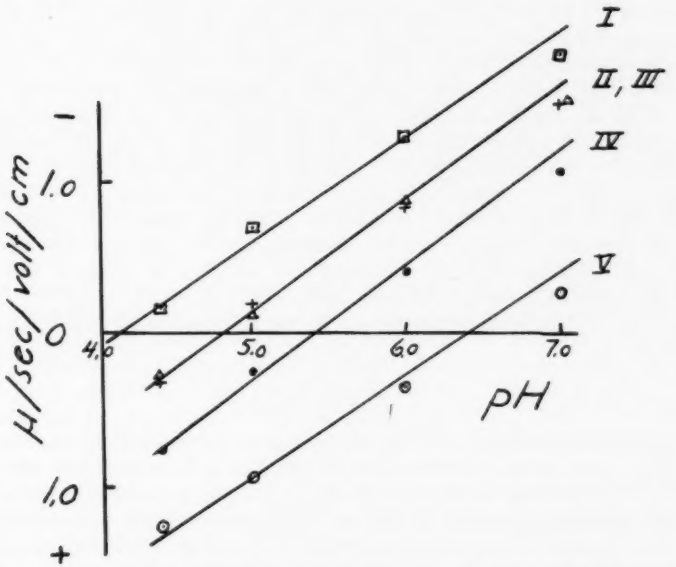

FIG. 1 pH-MOBILITY CURVE OF CHROME TANNED HIDE POWDER.

I. Cationic chromed hide powder (No. 1) in *acetate* buffer.
V. Ditto in *borate* buffer.
II. Anionic chromed hide powder (No. 5) in *acetate* buffer.
III. Ditto in *borate* buffer.
IV. Untreated hide powder (Blank).

partly at least, although the changes caused by the drying of the chromed stock will add further complications.

Electrokinetic potential. Professor S. M. Neale of the Department of Chemistry, College of Technolgy, Manchester, England, reported some difficulty of packing the finely divided hide powder to plugs of suitable permeability for the solution. Hence, a coarser type of tanned hide powder was supplied. The hide powder (no. 7) tanned by means of cationic basic chromic sulfate showed + 16 mv. charge in 0.01 *N* potassium chloride at pH 5.5, at which point the untreated hide powder was uncharged (iso-electric). The hide powder of anionic tannage (no. 8) carried a negative charge of 16 mv. under the same experimental conditions, according to Professor Neale. The iso-electric point of the cationic chromed hide powder was indicated to be about pH 7 and that of the anionic tanned stock at a pH of about 4.

Dyestuff technique. The fixation of the acid dyestuffs took place up to pH values of 7.0 – 7.6 for collagen of cationic chrome tannage and at pH values below 4.2 – 4.6 for the oxalate-tanned collagen (anionic type). The blank hide powder showed the range pH 5.0 – 5.6. By employing basic dyestuffs, the iso-electric points of the two types of chromed collagen fell at the values recorded for the anionic type of dyestuffs. In determination of the iso-electric point by the dyestuff technique caution must be taken not to use dyestuffs of ampho-ionic nature. The localization of the iso-electric point of chromized collagen by this technique points to the elevation of the pH value of the iso-electric point of collagen by incorporation of cationic chromium complexes with the protein, whereas the fixation of anionic chromium compounds shows the tendency of lowering the iso-electric point of collagen. The recent, important findings of Otto[9] regarding the behavior of variously treated chrome leathers towards dyestuffs agree with the present and the older findings[2–5]. Otto's contributions will be further discussed in the following section.

Discussion

The results from three different techniques of determining the iso-electric points of specimens of collagen tanned by means of cationic and anionic chromium complexes all point to the decrease of the strength of the anionic groups of collagen through its fixation of cationic sulfato-chromic complexes which may be considered as evidence for the view postulating the main attachment of this type of complexes to the carboxyl groups of collagen. The three techniques are also in complete accordance as to the inactivation of cationic protein groups through the irreversible attachment of negatively charged chromium complexes which is an indication of the basic protein groups to be chiefly involved in this reaction. In this instance coordinate reactions have been shown to occur[1,7]. This fixation which probably does not

alter the electro-chemical behavior of collagen is outside the scope of the present investigation.

The data given illustrate the easily occurring changes in the chromium complexes of cationic tannage leading to redistribution of the valency forces involved in the formation of the chrome-collagen compound. Since the issue at hand concerns the actual reactions taking place in tanning, it is imperative that the tanned collagen should not be *dried* during the preparation of the specimens for electrophoresis and also that buffers *without* marked affinity for chromium are employed in the electrophoretic determination. The marked effect of the acetate buffer on the hide powder tanned by means of sulfato-chromium complexes, containing an acido-group of moderate stability, and the absence of any effect of the acetate on the hide powder tanned by means of oxalato-chromiate, which is an extremely stable complex, illustrate this important point. Hence the speculations of Cassel and Kanagy in an attempt at finding an explanation of the peculiar effect of the amount of chromium fixed by collagen on its iso-electric point, suggesting different types of binding, are of no avail, since the explanation goes back to the data and hence in the last analysis to shortcomings of the difficult technique employed.

As a further illustration of the many unforseen complications in this field, the behavior of cationic chromed tanned leather upon drying is of immediate interest. Professor Neale received a sample of calf skin tanned by means of basic chromic sulfate (no. 4). After removal of protein-bound acid, the leather had been dehydrated in acetone and subsequently dried at 40°C. This stock showed a *negative* charge of 15 mv. at pH 5.5 or the same sign and magnitude of charge as the hide powder tanned by means of electronegative chromium complexes. Thus, the sign of charge was directing opposite to that of the *moist* hide powder tanned by the same basic sulfate, *not* dried before examination. The original moist chrome leather was iso-electric in the pH range 7–7.5 in tests for dyestuff affinity. By acetone-dehydration of the leather and final drying at 40°C, the iso-electric state was reached at pH 5–5.5. Hence, a displacement of the pH of the iso-electric point of two pH units resulted from this rather mild treatment. In this instance, the reason for the shift of the iso-electric point upon drying may be conceived as due to the incorporation of some of the charged basic protein groups into the chromium complex, resulting in their withdrawal from the ionic equilibrium. The primary and governing binding should remain intact, *i. e.*, the attachment of carboxyl ions of collagen to the cationic sulfato-chromium complex with the immediate following penetration of the carboxyls into the complex, establishing direct attachment on the chromium atoms of the polynuclear complex (covalent - coordinate binding) [18]. It is worthy of note that by drying the distance between adjacent collagen chains in the saltlink lattice, is reduced from 16 to 11 Å [19]. The interaction of ionic groups of the side chains with the chromium complex, linked by carboxyl groups of adjacent collagen chains, should hence be sterically favored by drying.

In some recent papers, Otto[9] has investigated the behavior of chrome leather, in the moist state and after various kind of aftertreatments and drying, towards anionic and cationic dyestuffs, including the chrome mordant type, *i. e.*, acid dyes capable of forming chelate compounds with chromium. His results obtained in the absence of buffers, are of fundamental importance for our knowledge of the nature of chrome leather. They have also an immediate bearing upon the problems under consideration and hence will be briefly discussed.

Otto has shown that complex-forming anions can easily change the positive charge of cationic chrome tanned leather into a negative charge. Further, it is found that moist chrome leather of cationic tannage does not fix basic dyestuffs at pH <6.5. However, upon drying fixation takes place from solutions with final pH values as far down on the pH-scale as 4.0 – 4.5. Leather treated in solution containing complex-forming anions, for instance, phthalate, shows also marked affinity for basic dyestuffs at pH values above 4. This implies that by drying of the chromed stock or by the fixation of anions by the chrome complex in the aftertreatment of the leather, the iso-electric point is shifted from pH $>$ 6.5 of the original moist leather to the pH range of 4–4.5.

In some further experiments, Otto[9] has shown that the acid dyestuffs of the metal-chelating type impart on fresh moist chrome leather the deep color of the internal complex salt of the particular dye with chromium (chrome lake)[20]. On the other hand, upon drying the leather carefully, not impairing its water uptake by a forced drying; and further by treating the moist chrome leather with solutions of salts of complex-forming anions, the leather takes on the less intense color of the acid dyestuff, *i. e.*, the shade obtained on wool. The mordanting effect of the chromium complexes, is absent. By the changes taking place in the chrome complexes these are made non-reactive and do not coordinate. Otto concludes that by these treatments of the leather radical changes are induced into the fixed chromium complexes in the direction of the formation of anionic complexes with accompanying lowering of the iso-electric point. Otto's clarifying researches substantiate the findings of some twenty-five years' standing and also the results reported in this paper.

The impact of these results and earlier findings[10] make a reconsideration of the concept of the mechanism of the cationic chrome tannage imperative. The initial reaction is an ionic interaction of cationic chromium complexes, such as $(Cr - O - Cr - \underset{2}{\overset{SO_4}{}} - Cr - O - Cr - \underset{2}{\overset{SO_4}{}})^{n+}$ with the charged carboxyl groups of collagen, the sulfate ions being compensated by the ammonium–ions. The carboxyl groups, having a great tendency to complex formation and for a direct attachment to chromium, penetrate into the coordination sphere,

forming a covalent-coordinate bond. Since several chromium atoms are present in large chromium complexes, and in view of the secondary aggregation of the fixed chromium complexes by further hydrolysis, possibilities may be at hand for a multipoint interaction of one chainlike chromium complex with several carboxyl ions of the collagen lattice, resulting in the linking of adjacent protein chains by a few strong bonds by means of the chrome bridge. Shuttleworth's conductivity data for gelatin solutions containing chromic salt point to the inactivation of carboxyl ions as the main reaction [18]. This type of crosslinking a polynuclear chromium by means of two or more carboxyl groups on adjacent protein chains, accounts satisfactorily for the chemical behavior of chromed collagen, particularly the increased reactivity of the basic protein groups resulting from the chrome tannage [21]. In view of the new data of the free carboxyl groups, more than twice the earlier accepted value [22], previous objections based on spatial and stoichiometric considerations are largely removed.

The amino groups are probably not concerned in the tanning process proper, and their participation in the crosslinking does not appear essential. The possibility of secondary involvement of basic groups or other coordination-active groups upon ageing, drying etc. should not be lost sight of. It is particularly the amino acid residues carrying hydroxy groups (hydroxy-proline and serine) which possess marked coordinate valency activity. Since the total amount of these hydroxy acids, expressed in equivalents, is practically twice the amount of cationic protein groups [22], the spatial and chemical consideration would favor the hydroxy residues as functional groups. Further, the hydroxy group, *e. g.*, in glycolic acid, facilitates the formation of chelating compounds with metals, for instance copper [23]. Since chelating should occur between chromium, as an electron acceptor, and protein groups functioning as electron donors, the hydroxy groups of collagen fulfills the latter requirement but not the ammonium-*ions*, the form in which the amino groups exist at the pH prevailing in chrome tanning of pickled pelt with moderately basic chromic salts; the number of free electron-donating NH_2-groups being negligible. [24].

Summary

The values of the iso-electric point of hide protein tanned by means of basic chromic sulfate (cationic) and by means of sodium-diol-tetra-oxalato-chromiate (anionic) have been determined by three methods:

1. Micro-electrophoresis, employing specimens *not dried* after completed tannage and buffer solutions *without affinity for chromium*.

2. The electro-kinetic technique (Neale) and

3. The dyestuff fixation as a function of pH.

The three methods gave concordant results, showing that:

1. Cationic chrome tannage, *i. e.*, the regular type of chrome tanning, elevates the iso-electric point of collagen from pH 5.5 to pH 6.5 – 7.5.

2. Anionic chrome tannage shifts the iso-electric point of collagen to pH 4 – 4.5.

By employing an acetate buffer, hide powder tanned by means of cationic chromium complexes is iso-electric at pH 4.2. A reversal of the charge of the fixed chromium complexes evidently is induced by the penetration of acetate groups into the polynuclear chromium complexes. The iso-electric point of oxalato-tanned collagen is not affected by the type of buffers employed. Earlier findings of Theis and of Cassel and Kanagy which are contrary to the figures of the iso-electric point obtained by the dyestuff technique are vitiated by unsuitable choice of buffers and the use of chromed hide powder which has been dried.

By drying of hide powder of cationic chrome tannage, the iso-electric point is shifted about two pH units towards the acid side. Otto's finding that by the treatments mentioned the chromium complex acquires a negative charge is discussed. His findings substantiate the results of this investigation.

The concept of chrome tanning, postulating the stabilization of collagen by the formation of stable crosslinks between adjacent protein chains through the carboxyl groups, entering into direct combination with the chromium atoms of the polynuclear complex is strengthed by the data presented. It is admitted that a number of recent findings are difficult to reconcile with the internal complex salt hypothesis of chrome tanning, assuming acidic as well as basic protein groups to be involved. The participation of hydroxy-amino acid residues (hydroxy-proline and serine) as coordination centers in secondary reactions appears more reasonable than the function of cationic protein groups as coordinators, from chemical and spatial considerations.

Acknowledgment

Without the kind and generous cooperation of a number of colleagues outside the chosen specialty, this investigation could not have been accomplished. The author takes great pleasure in expressing his sincere thanks to Dr. H. Svensson, Upsala, Professor N. Grale'n and Mr. B. Olofsson, Gothenburg and Professor S. M. Neale, Manchester, England for their invaluable service. The inspiring contact with the author's old friend, Dr. G. Otto, Ludwigshafen, Germany, is also gratefully acknowledged.

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ABSTRACTS

National Water Resources Policy as Related to Stream Pollution. By L. R. Howson. *Sewage and Industrial Wastes*, **24**, 222 (1952). The author contends that a sound national water policy as related to stream pollution should recognize that: 1. Although approximately two-thirds of the urban population of the United States is now provided with sewage treatment facilities, serious stream pollution persists. 2. Excellent progress has been made in waste treatment, both municipal and industrial, under the present system of controls. Such controls are believed adequate and should be continued. 3. Stream pollution should be controlled at the lowest practicable level of government having jurisdiction over the stream. 4. Sewage treatment should be provided by and at the expense of those contributing the pollution. In general, municipal waste treatment can be provided at a cost of approximately 1 cent per capita per day. 5. Federal loans should only be made on projects of limited benefit on terms which are fair to all other citizens. This requires that the loan be

fully repaid within a period shorter than the life of the facilities and that the interest be sufficient to cover all costs incurred by the Federal Government, including administration. 6. Greater speed in accomplishing the complete cleanup will be realized if the approval of future construction is not predicated upon questionable fringe reclamation benefits. Pollution abatement and waste treatment are essentially economic problems. 7. Control of pollution and the responsibility for its correction now lie primarily in the states, where it should remain. The Federal Government should confine its efforts to administration of existing laws, to research, and to guidance to the states of political subdivisions in the formulation and enforcement of regulations having as much uniformity as is consistent with the variable conditions encountered.

Evaluation of Stream Pollution. By L. L. Hedgepeth. *Jour. Am. Water Works Assn.*, **43,** 1, 55 (1951). Through *Sewage and Industrial Wastes*, **24,** 243 (1952). A representative of industry presents his viewpoints in this paper on the stream pollution control program. Due to the extensive costs involved for treatment plant construction and maintenance, the author insists that nothing short of absolute legal requirements will get the job done. Much of this paper covers the opposition to standards for treatment. This is based on lack of a proper yardstick for measurement of industrial pollution and on the variable effect of industrial wastes on a stream. For measurements of pollution the merits and weaknesses of the biochemical oxygen demand, the new bio-assay techniques, and chemical and physical tests, are discussed. In contrast, it is stated that no one test is applicable and that considerable specific experience and mental alertness are needed to judge each situation on its own merits. In other words, critical appraisal of stream pollution is deemed to be desirable instead of using general criteria for all situations. In conclusion, the progress made by industry to date is cited. Much more has been accomplished than appears on the record, as many leading industries have accepted waste treatment as a necessary part of new plants or expansions. Technical men in the industry are also using their special skills and process knowledge to solve the varied problems of industrial pollution, and this information is being freely exchanged at heavily attended and unpublicized conferences of industry.

Ropiness In Tan Liquors. By G. Cane. *J. Soc. Leather Trades' Chemists*, **35,** 355 (1951). Ropiness is fairly widespread in catechol liquors not treated with antiseptic and where tannage is carried out at natural value of the extract, say from pH 4.5 in the stronger liquors to pH 6 at the tail. Appearance of ropiness is accompanied by a large increase of viscosity and reduction of the penetration to almost zero. The phenomenon bears signs of bacterial action but previous attempts to reproduce it by inoculation were not successful. However, such a procedure was successful in this work. During this study it was noticed that a ropy liquor could be formed by dissolving the acetone insoluble fraction of mimosa extract in cold tap water and letting it stand 7-14 days. Ropy liquors used for inoculation were prepared in this way. Occurrence of ropiness in suspender liquor and in 100 degree Bk. mimosa extract dissolved in cold water demonstrated that the presence of hides in the liquor is not necessary for the growth of the organism. Since tannin precipitates both gelatin and agar, 2½ per cent agar was dissolved in detannized mimosa solution of original analytical strength. This medium was sterilized and poured into sterile Petri dishes. Plates so prepared were inoculated over the entire surface with the ropy inoculation liquor mentioned above. Incubation was carried out at 30 degrees C. for three days, some aerobically and some anaerobically. The former were facultative. The latter were not and were discontinued. In all, five strains of yeast and two of micrococci were isolated and sub-cultured. The micrococci produced ropiness, when incubated at 30 degrees for 14 days. The yeasts did not. The strains were typed as Micrococcus Ureae and Micrococcus Varians. Both

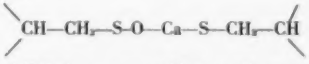
organisms are capable of utilizing inorganic nitrogen and phosphorous and simple organic compounds as a source of carbon. Though capable of growth at pH 4.5, they are less resistant to acid than the lactic and acetic acid producing bacteria found in sugar rich pyrogallol liquors. The carbon compounds of mimosa may be divided into three groups: tannins, phenolic non-tans and glucose. All three were prepared from mimosa extract and also a medium containing the essential inorganic salts. Mixtures of these were made up, sterilized and inoculated with M. Varians. The results were as follows: Glucose plus salts, growth but no ropiness. Phenolic non-tans and salts, both growth and ropiness. Tannins and salts, neither growth or ropiness. Resin treated non-tans only (treated with base exchange resin), neither growth or ropiness. Resin treated non-tans and salts, both growth and ropiness. It is significant that, while growth occurred in glucose, it did not turn ropy. Further it was found that, although the non-tans as prepared showed no tannins, due to oxidation or other effect during manipulation a positive tannin test was found at the end of the procedure. A series of tests with 0.2 per cent glucose and various percentages of tannins showed that tannins inhibit the growth of the organisms but do not prevent it in weak concentrations. In fact, apparently some tannin is essential for the ropiness to develop. If no tannin is present, there will be growth but no ropiness. Tests with a strain of yeast grown with the organism indicated that the yeast provides substances which enhance bacterial growth. It seems likely that, as a liquor works its way down the yard, yeasts will grow first until the sugars are exhausted and then, as tan diminishes, the bacteria will commence to grow and ropiness make its appearance. The ropiness is apparently the initial stage of a pure gel formation, as evidenced by a gel consistency of the residue of filtered ropy liquor and formation of a gel in a ropy growth on four months' standing. R. H. T.

The Real Densities of Chrome and Vegetable Tanned Leathers. By C. D. Pomeroy and R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **35**, 360 (1951). The apparent density of leather is the ratio of the mass to the volume bounded by its outer surfaces. The real density is the ratio of the mass to the volume occupied by the leather itself. Measuring the real density is difficult because of the porous nature and the tendency of leather to adsorb or absorb any medium in which it is immersed. The authors present the following pertinent facts: (a) The surface area of the leather fibers is of the order of 10^4 cm^2 per gr. This is not large enough to cause difficulties due to irregularities of molecular dimensions. (b) There is no evidence that leather surfaces possess capillaries of molecular dimensions as in charcoal and silica gel. But the crystalline lattice of collagen is relatively open in structure. It is not unlikely that small molecules can penetrate into the disordered parts of the fiber even if the fluid is relatively inert. (c) Molecules may be able to penetrate into the crystalline region. There is X-ray evidence that water does so readily. (d) If the displacement fluid is gaseous, it may adsorb on the fiber surfaces giving too small a leather volume. This may be avoided by using an inert gas such as helium. (e) If true that the fluid can penetrate the crystalline lattice, it is doubtful whether any useful meaning can be attached to such expressions as "the volume not accessible to the fluid" or "its effective density within the solid," since neither quantity can be measured separately. These conclusions show that, whatever fluid is chosen for the measurement, the results are not likely to be simply related to the volume of the solid material, if volume is regarded as a geometrical concept. There is no justification for accepting the real volume as correct, as measured by any particular fluid. The adjective "real" in this sense is misleading. Nevertheless it is used in this paper because so well established. Five methods for measurement of real volumes are given. Method one is by displacement of liquids. The degreased sample was dried in a vacuum desiccator and weighed in air. It was then exhausted and filled with the liquid to be used by allowing it to be drawn in over the exhausted sample. It was then weighed in the liquid.

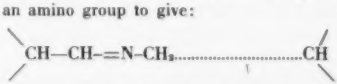
All weighings were done in a room with controlled temperature. The volume is calculated from the two weights and the measured density of the fluid. The second method, based on pressure and volume measurements in accordance with Boyle's law, was found unsatisfactory because, although carried out in a constant temperature room, the heat of the operator's body caused serious errors. The third method was essentially a duplicate of the first method, substituting gases for fluids. However, the upthrust of the gas was so slight that even a specially constructed microbalance did not give satisfactory results and this method was also abandoned. In the fourth method the leather specimen is placed in an evacuated chamber of known volume and a gas admitted until the pressure reaches a specified value. Under these circumstances the volume of the gas admitted is the difference between the volume of the chamber and the real volume of the specimen. An apparatus is described for using this method. The fifth method is one for measuring the volumes of leather samples containing moisture, and conditioned to equilibrium with atmosphere of known relative humidity. A procedure, using the apparatus described in method four, for accomplishing this is given. It was found that the moisture content of leather at any given R.H. varied with the direction of approach. If the direction was from higher to lower, the moisture content was greater than if the same equilibrium was reached from lower to higher, thereby exhibiting hysteresis. The authors were interested in determining whether the volume of leather shows a similar hysteresis effort. Using air as a displacement medium it was shown that the specific volume of vegetable tanned leather showed a hysteresis when measured in ascending and descend- R.H. Chrome tanned leather did not show it. The hysteresis loop was in reverse of what it would be expected to be, the curve for ascending moisture lying above instead of below. The apparent hysteresis is thought to be due to adsorption of oxygen by vegetable tanned leather. In any case air should not be used for measuring specific volume of vegetable tanned leather. When nitrogen was substituted, neither chrome or vegetable tanned leather showed any hysteresis. Thus it is concluded that the volume of leather at any moisture content is the same, regardless of whether approached from greater or less moisture content. When the densities of chrome and vegetable tanned leather are plotted against moisture content, chrome leather shows a density increase, between zero and 12 per cent moisture, from 1.44 to 1.51 and then a rapid decrease to about 1.38 at 33 per cent moisture. Vegetable tanned leather starts with a density of about 1.49 shows a slight increase up to a moisture of about 6 per cent and then drops, finally reaching about the same density as chrome leather at 33 per cent moisture. For both types of leather the density, calculated from measurements based on displacement of nitrogen gas, lies in the range of 1.51 to 1.39 gr. per ml., the actual value depending upon the moisture content as well as such factors as the nature and extent of tannage. Other gases exhibited some changes. Volumes of leather are largest when helium is used. Smaller volumes found with hydrogen, nitrogen, oxygen and air are probably due to slight adsorption of the molecules on the fiber. Real volume measured by displacement of liquids having molecules of various sizes are practically the same for all those used. Liquids used were benzene, toluene, heptane, cineol, liquid paraffin, butyl phthalate, tricresyl phosphate, xylene, oleic acid, castor oil and triacetin. There is no evidence that the density measured by liquid displacement depends upon the molecular size as represented by the parachors. The volumes measured by liquid displacement are larger and densities smaller than those obtained by gas displacement. The ratio of densities by air and liquids is about 1.12 for chrome leather and 1.13 for vegetable tanned leather. The grain layers of vegetable tanned leathers have higher real densities than the corium, probably partly caused by differences in degree of tannage of grain and corium. Measurements, by gas displacement, of the real volume of vegetable tanned leather, before and after addition of oil, gave no indication that the oil passes into the fibers themselves; and the close agreement of the volumes measured by displacement of a number of liquids points to the conclusion that the oil added to leather remains on the surface of the fibers and in the interfibril-

lary spaces. If so, the function of the oil added in operations such as oiling, currying and fat liquoring is to act as a lubricant and prevent adhesion of one fiber to another. Unlike water, which penetrates into the interior of the fiber and changes the elastic properties of the tanned collagen, the oil has an influence on their surfaces only. The real densities of dry collagen from hide and hide powder are 1.41 and 1.39 gr. per ml. respectively. The lower value of the hide powder is probably due to some disorganization of the structure brought about during its preparation. The measured density can be compared with that to be expected if collagen is assumed to have a structure such as has been suggested; the measured and predicted densities differ by an amount that appears far too large to be the result of experimental error. The predicted density, calculated from X-ray and chemical data is 1.18. R. H. T.

Reactions of Keratin In Alkaline Solutions. By R. McKay. *J. Soc. Leather Trades' Chemists,* **35,** 382 (1951). The ability of folded keratin chains to contract further (supercontract) has been used for study of the unhairing of hides. Speakman found that human hair boiled in a 5 per cent solution of sodium bisulfite could be supercontracted to the extent of about 24 per cent. He also found that prior treatment with 0.1 N barium hydrate, for varying lengths of time, led first to a diminution in the ability of the hair to supercontract and later to a partial recovery of the property. In this study hair from an ox tail was degreased, measured, immersed in saturated lime water for various periods, boiled for 60 minutes in 5 per cent bisulfite solution, dried and supercontraction measured. Supercontraction beginning at about 24 per cent at zero time, decreased to zero contraction in 3 hours. In other words the lime treatment of over three hours immunized the hair to the supercontracting action. Solutions of sodium sulfide 0.01–0.15 per cent were used similarly to the saturated lime water. The lower concentrations merely delayed the immunization. The higher concentrations prevented it. Speakman found that immunization with caustic soda was much slower than with divalent alkali. This study demonstrated that in the presence of sufficient alkalinity very small concentrations of divalent ions are sufficient to immunize hair. The presence of unionized calcium in the immunized hair was demonstrated. In the absence of sulfide the initial hydrolysis of the disulfide bond is followed partly by the formation of metallic links:



and partly by the loss of H_2S from some sulfenic acid groups, followed by linking of the residual aldehyde with an amino group to give:



Both these links are stable to alkali and reducing agents, and explain why, if a hide is immersed for several hours in straight lime, the subsequent addition of sulfide fails to accelerate unhairing. If sulfide is present in the solution initially, the sulfenic acid groups will be reduced, thus preventing the formation of either type of link. R. H. T.

Committee On Oils, Fats and Waxes. XVII. Analysis of Moellon Degras, Sod Oil, etc. By D. Burton and G. F. Robertshaw. *J. Soc. Leather Trades' Chemists,* **35,** 391 (1951). The confusion in the nomenclature of degras complicates the subject. Procter describes the production of moellon by squeezing skins which have been tanned by whale, seal and liver oils. For currying, this is mixed with further fish oils, tallow and sometimes wool-fat and then sold as degras. The English sod oil is obtained from pelt tanned with liver oils by

scouring with alkalies and recovering by acid treatment. It consequently may contain soaps. McLaughlin and Theis point out that wool grease or moellons are often referred to as "degras." According to them manufacturers of leather oil products are quite clear in the use of these terms and the nature of the material that each term designates. "Natural Moellon" is a by-product of chamois tanning. Sod oils used in England come under this category. "Artificial Moellons" are products of the transformation of marine oils: (a) Oxidized or blown oils, (b) partly sulfated or hydroxylated oils, (c) and or treated with water in oil emulsifiers. According to Thuau and Lisser, "Degras" is a mixture of moellons, oils, fats and oxidized fatty acids. Nevertheless "degras" is the French name for fish oil that has been used in chamoising. The constituents of sod oil are water, ethyl ether insoluble matter, total fatty matter, unsaponifiable matter, "oxidized" fatty acids, total "non-oxidized" light petroleum soluble fatty acids, inorganic compounds as per cent ash, volatile compounds, water soluble compounds and rosin, which may be present. Recommended methods for determination are given for each. R. H. T.

Recent Advances in the Study of the Composition of Basic Chromium Salts. Part II. By E. Mitchell. *J. Soc. Leather Trades' Chemists*, **35**, 397 (1951). A published paper by Atkin and Chollet showed that boiled and cooled chrome alum solutions in increasing concentrations exhibited increasing amounts of complex bound sulfate groups and a stoichiometrically decreasing amount of hydroxyl groups. The aim of this research was to obtain explanation of changes taking place in complexes of chrome alum solutions under influence of addition of alkali, paying special attention to the effect of time. It is generally accepted that reactions of trivalent chromium salts may be resolved into hydrolysis, olation and migration of acid radicals into or out of the complex. They follow one another quickly and are all reversible and interdependent. The hydrolysis is regarded as the dissociation of hydrogen ions from complex bound water molecules. For every free hydrogen ion there is a hydroxyl attached to the chromium atom. Stiasny has shown how hydrogen ion concentration in a solution of cold dissolved chromium sulfate increases on aging, and how the reverse is true for boiled and cooled solutions. Olation is the condition in which a hydroxyl is attached to two chromium atoms instead of one. Olated hydroxyls are not titrated with acid. Acid radical migration depends upon their nature as well as the condition of the complex. It has been shown that, in basic chrome alum solutions, some sulfate groups are attached covalently to the Cr atom, others electrovalently associated with the complexes. In the outer solution there are free sulfate radicals as well as free hydrogen and potassium ions. Thus the number of possible combinations is great. The analysis of chrome solutions were carried out according to standard procedure with slight modification. The ionic sulfate radicals were precipitated as benzidine sulfate then hydrolyzing this compound in the presence of sodium hydroxide. The sodium hydroxide thus titrates the sulfate ions as if they belonged to a strong acid. The degree of olation, expressed as:

$$\frac{\text{No. of olated OH/Cr}}{\text{Total OH/Cr}} \times 100$$

was found as follows. Each of the compounds investigated was produced by the addition of a known amount of alkali. By titrating such a compound with acid and determining the equivalents of acid necessary to bring the solution to pH 3.3, the number of olated groups was obtained as the difference between the equivalents of acid thus added and the equivalents of alkali originally added. Precautions necessary for such titrations are given. Analyses were made of basic chrome alum solutions prepared from boiled and cooled chrome alum. The reaction reaches equilibrium after 15 minutes. At 10 g. per liter concentration the composition of the complex is: $[Cr_4(OH)_8(SO_4)_2(H_2O)_{12}]^{+++}\ 3SO_4^{--}\ 3H^+$.

Immediate back titrations with acid were made of freshly prepared solutions to which differing amounts of sodium hydroxide had been added. The distribution of sulfate groups was determined. Similar experiments were performed with cold dissolved chrome alum in which the complexes correspond to $2[Cr(H_2O)_6]^{+++}\ 3SO_4^{=}$. In both groups of experiments a stoichiometric relationship was found between formation of olation hydroxyl groups and entry of sulfate groups into complexes. In both groups similar back titrations were made after several days aging. A similar final equilibrium stage to that obtained by aging was reached by boiling chromic alum with varying amounts of sodium hydroxide for 15 minutes. To study the effect of neutral salt concentration, a boiled and cooled solution of chrome alum was treated with three equivalents of sodium sulfate per Cr atom and subsequently titrated with NaOH. This titration curve was identical with that for untreated basic chrome alum and NaOH, except for slight change in the portion of the curve which represents the titration of free sulfuric acid. The following generalizations are drawn. On addition of alkali a certain amount of olation takes place at once, but in no case does olation reach equilibrium value immediately, except at the lowest degree of basicity. The degree of olation is higher the smaller the amount of alkali added. In the ultimate stage, i.e., when chrome alum and NaOH have been boiled together, 100 per cent olation is reached only when there are two, or less, hydroxyls per chromium atom. Experimental results of this paper show that, when hexaaquo chromium complexes are treated with alkali, the formation of an olated hydroxyl group is accompanied by the entry of a sulfato group into the complex. If, however, the concentration of the alkali is such that two olated groups per chromium atoms are formed, sulfate groups again leave the complex. This is the case with the basic solutions prepared from boiled and cooled chrome alum. The degree of olation increases with aging. The stoichiometric distribution of sulfate and olated hydroxyl groups suggests that both valencies of the sulfate group are involved in a combination with the chromium atoms. The evidence obtained supports the suggestion that the prevalent arrangement of olated hydroxyl groups and complex bound sulfate groups is in the form of the ring structure originally suggested by Atkin. The proportion of complex bound sulfate to ionic sulfate is governed by the ratio of coordinated water molecules to free water molecules in the solution. R. H. T.

A Machine For Measuring the Run of Gloving Leather. By R. H. Hall and R. G. Mitton. *J. Soc. Leather Trades' Chemists,* **35,** 411 (1951). A gloving leather, when stretched in one direction, should contract along lines at right angles to the direction of stretch. This is necessary for a snugly fitting glove. This property is known as "run" and can be assessed by an experienced workman from measurements taken after he has stretched the skins by hand. Such a method can hardly be considered satisfactory since there is no measure of the forces used. Some attempts to get exact and uniform data have been made, using a flexometer, but were not satisfactory. This paper describes a machine specially designed for the purpose. In hand stretching the skin is stretched parallel to the backbone and the width (w_o) measured. It is then stretched directly across the backbone and the width (w_1) measured. Run (R) is calculated from the equation $R=100(w_1-w_o)/w_o$. As this method seems satisfactory, apart from the uncontrolled and only approximately known forces applied, the function of the machine is to allow a similar method with known force application. The construction and calibration of the machine are described in detail. It was found that lower stresses must be used with the machine than by hand. Even at the maximum safe load, which was found to be 80 pounds for gloving skins, the run determination was of consistently lower value for the machine than for the hand stretching. However the tests made showed that the property measured by the machine and hand test is essentially the same. The machine is therefore suitable for the purpose. R. H. T.

The Abrasion of Sole Leather. A Comparison of Rates of Wet and Dry Abrasion on Two Abrasion Machines. By R. G. Mitton and R. H. Hall. *J. Soc. Leather Trades' Chemists*, **36,** 4 1952). During the war efforts were made to correlate abrasion tests with rates of wear for army shoes but the correlation was so unsatisfactory that discontinuance of abrasion tests was recommended. Subsequent work has shown that the wear tests were themselves subject to serious errors. It follows that the poor correlation might have been due to the method used in assessing the comparative wear. It is also true, however, that results obtained in abrasion tests at different laboratories were quite inconsistent in themselves. Obviously, unless consistent results can be obtained by different workers with the same style machine, the data will have little value. Also machines of different design, if suitable for the work, should give consistent results. The object of this study was to secure further data with two quite dissimilar type machines. Samples were obtained from the official sampling position in 17 bends, each from a different tannery; and a number of specimens from each bend was tested on each machine. Since sampling fluctuations will inevitably introduce disturbing factors, it is necessary to determine whether disagreement of results is explicable due to sampling errors and abrasive variation, or whether incomplete agreement indicates that one type of machine favors certain leathers at the expense of others. The experiments were designed to answer this question. With each machine both wet and dry abrasion can be accomplished and both were used. One machine was rotary, one reciprocating. Both are described in detail. The same grade and make of abrasive and the same load weight were used on both machines. To reduce to a minimum the effect of non-homogeneity of the surface layers of leather the rate of abrasion was measured on the middle third of the leather thickness. Detailed data of the results obtained and method of interpretation are given. The experiments show that present knowledge concerning the abrasion testing of wet leather is far from adequate and that further work on this is necessary. In this study the correlation between the two machines was completely negligible in wet leather abrasion. Whether this is due to differences between the water uptake of the specimens, to clogging of abrasive by the fiber removed, or to some other factor is not known. Better results were obtained in the dry abrasion tests, the two machines giving results in fair agreement. Further the agreement between the two machines is about as good as can be obtained in two sets of tests with one machine. Nevertheless the position is not satisfactory, since the ranking of a set of leathers depends upon the details of the test to a somewhat greater extent than would be expected from similar measurements of neighboring specimens from one and the same leather. It is not clear whether this is due to inadequate control of some factor in the conditions of test. R. H. T.

An Apparatus for Measuring Color Fastness of Light Leathers to Wet and Dry Rubbing. By G. R. Nice. *J. Soc. Leather Trades' Chemists*, **36,** 15 (1952). Dye finishes should be resistant to wet and dry rubbing. This paper deals with a method of determining the fastness of dye in light leather against both wet and dry rubbing. The apparatus used consists essentially of a 3-inch radius brass drum with a variable speed drive giving a range of 5 to 20 r.p.m. The leather sample holder has the same curvature as the drum and rests upon it from above. The arc of contact is 3/4 of an inch. Attached to the sample block is a load platform on which weight may be placed to give load pressure on the sample. A 60-watt lamp is placed 6 inches from the drum for illumination. At that distance it did not heat the drum surface appreciably. To carry out the test a length of clean white cotton tape 1½ inch wide, 70-80 warp and weft, is wrapped around the drum and threaded through a small slit in the drum. The ends of the tape are clamped to a small inside drum. A load is placed on the platform, the counter set at zero and rotation set at any desired speed within the available range. It was found that different observers preferred somewhat different speeds. As the final result depends upon the number of revolutions such speed variation

has no effect on values obtained. When a trace of color is seen on the cloth the motor is stopped and the number of rotations observed. A wet test is similarly run, using a wet cloth kept wet by dropping distilled water on the cloth at about one drop per revolution. The effect of load change was studied. It was found that, in the lower range, small weight changes had a marked effect on required revolutions; but, as the load increased, the effect was greatly reduced. Log of loads plotted against log of revolutions gives a straight line. Therefore, expressing weight as (W) and revolutions as (R) the equation of the curve is $R=aW^n$, where (a) and (n) are constants. Since it is necessary to choose a fixed load, 2 kg. was selected for dry leather and 300 gr. for wet. The "rub number" of a leather is defined as the log (to base 10) of revolutions multiplied by 100. The advantages of this system of measurement are discussed. The machine gives satisfactorily reproducible results, both in replication by an individual and duplication by different observers. Even among the relatively small number of leathers examined, variations of over 100 times in dry fastness were found in leathers visually similar. Even greater variations were found in wet fastness.

R. H. T.

The Hydration of Collagen and Leather. By C. H. Spiers. *J. Soc. Leather Trades' Chemists*, **36**, 20 (1952). Collagen is a hydrophylic colloid which putrefies when it has absorbed water. Tanned collagen is considerably less hydrophilic. A characteristic property of leather is that the fibers are free from one another making the leather flexible. Water swollen fibers adhere on drying, creating stiffness. A tanning agent must dehydrate the fibers to such an extent that they no longer adhere on removal of solvent by evaporation. This can be accomplished by such dehydrating agents as alcohol and concentrated salt solutions as well as normal tanning agents. To achieve a leather resistant to water the agent must make the fiber permanently incapable of taking up water. Various investigators have proposed that the effect of tanning is largely due to the change in the hydrophilic property of the collagen, pointing out that all tanning agents convert the hydrophilic groups of collagen to groups which have less active polarity for water. Further the physical properties of leather, such as tensile strength and density, vary with the moisture content which in turn depends upon the R.H, and temp. of the atmosphere. In this work the effect of varying water content on the real densities of collagen, vegetable tanned leather and chrome leather have been studied. The materials used were: (1) degreased and partially dehydrated collagen from delimed ox hide, washed and buffered to the isoelectric point, pH 5, (2) vegetable tanned leather, by mimosa bark, dried at 100 degrees C., (3) one bath chrome tanned leather dried at 100 degrees C. The real volumes of the dried specimens were found by means of the author's direct reading columenometer described in a previous paper. They were then allowed to rehydrate in air and finally over water, the weights and real volumes being taken at intervals. The real density of dry collagen was found to be 1.22. It gains 42.3 gr. of water per 100 gr. dry collagen, increasing in real density to 1.40 and changing in volume from 81.91 ml. to 101.51 ml. Vegetable tanned leather had a real density of 1.38. It gained 24.42 gr. of water per 100 gr. dry leather, changing in volume from 72.2 to 86.9 ml. and increasing in density to 1.43. Dry chrome tanned leather had a real density of 1.21. It gained 39.87 gr. of water per 100 gr. dry leather changing in volume from 75.2 to 93.9 ml. and attaining a real density of 1.49. The most interesting feature of the results observed is that the increase in volume is much less than the volume of the water taken up, the water undergoing a compression on absorption. The compression is very great initially, gradually diminishing as more water is taken up. There is a clear indication that the tanning agent alters the affinity of the collagen for water. Curves are given plotting the compression of water against the weight of water absorbed per 100 gr. of dry collagen. These all show a high apparent density of absorbed water at low weights of water absorbed, decreasing quite rapidly with increased water and tending to flatten out above 10 per cent absorption. Col-

lagen shows the greatest initial compression and vegetable tanned leather the least, with chrome tanned leather between, showing that vegetable tannin is more effective in reducing the affinity of collagen for water than chromium salts. This is in accordance with modern ideas. According to Atkin collagen contains 28 molecules of the diamino acids, arginine and lysine, which have a great affinity for water, and 23 molecules of the dibasic acids aspartic and glutaric, which have slight affinity. Since vegetable tannin is supposed to combine with the amino groups and chromium salts with the carboxyl groups, the latter would be expected to have less effect on the water affinity, as demonstrated. R. H. T.

Pine Bark Tannin II. Change of Alcohol-Precipitation Number During Fractional Extraction of Pine Bark. By A. Haglund. *Das Leder*, **2**, 205 (1951). Liquor samples were taken simultaneously from each unit of a 7-unit battery leaching fresh pine bark. After analysis, the liquors were concentrated in vacuum to 10 per cent total solids for determination of alcohol precipitation number (AP No.). The results were as follows:

Extraction number	1	2	3	4	5	6	7
Alcohol precipitation number	28.2	35.0	41.6	47.1	52.7	55.3	58.7
Purity of fraction II (not precipitated)	53	60	59	57	53	41	—
Purity of unfractioned extract	55	62	60	57	53	44	36

Laboratory extraction of 4 kilograms of bark with 10-liter portions of pure water gave the following results:

Extract No.	1	2	3-5	6-13
Purity	46.7	53.3	66.4	52.7
Alcohol precipitation No.	16.4	15.2	26.1	60.1
Viscosity, Cp at 15% T.T.	2.08	2.42	5.54	9.74
Tan value	72.6	80.2	76.4	57.9
Combining value	34.1	46.0	51.8	38.9

The results show that Fraction I (precipitated by alcohol) is relatively difficult to extract. Either AP No. or viscosity can be used to measure relative particle size. There is a relation between tan and combining values on one hand and AP No. and purity on the other. Extracts No. 3-5 with average AP No. and high purity had the greatest combining value while extracts No. 6-13 with high AP No. and low purity had the lowest tan and combining values. After the 13th extraction the spent bark was extracted with 2.5 per cent sulfite and 2.5 per cent bisulfite. The resulting extract had low tan and combining values, showing that sulfited phlobaphenes can not be used alone for tanning. I. D. C.

Practical Experience With Paste Drying. By F. Henaker. *Das Leder*, **2**, 217 (1951). Practical aspects of pasting, drying and washing to remove remaining paste are discussed. Paste should be easy to prepare, have good adhesion, but should not penetrate the grain nor contain insoluble matter or grit. A single type of paste will not serve all purposes because various leathers or parts of a skin do not have the same moisture content and absorptivity. A paste made of 1,000 parts of carob bean pods, 2,000 parts glucose, 600 parts sulfonated neatsfoot oil and made up to 15,000 parts gave good results for some time, then failed in humid weather. Brown leather behaves better than blue, green or red colored leather. I. D. C.

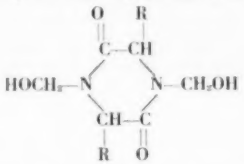
Brine Preservation of Cattle Hides. By E. J. Strandine. *Das Leder*, **2**, 220 (1951). A brief description of the Swift Co. brining process. I. D. C.

Observations on Pasting of Chrome Leather. By W. Wudich. *Das Leder*, **2**, 242 (1951). Leather is usually dried by a countercurrent method, in which dry air is introduced at the dry leather end of the tunnel and moves toward the wet leather entering the tunnel. Paste drying differs in that the relative humidity must remain at from 50 to 60 per cent throughout the process with the temperature held between 40 and 50°C. Relative humidity must never be as low as 40 per cent, with the exception, that it may be 20 per cent in the first two units, where the leather is wet and the plates are cold. If the humidity is too low, the edges of the leather loosen, become too dry and interfere with airflow and prompt drying of the remaining leather. The leather must be well tanned, must contain not less than 2.5 per cent chromium oxide and must be well oiled on the surface. The ratio of unsulfonated to sulfonated oil should be between 1:1 and 1:2 but the former must not be train oil. I. D. C.

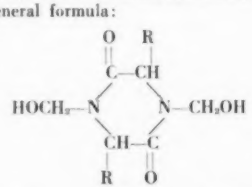
Tannin from Lignin Sulfo Acids. By G. Mauthe and M. Meister. *Das Leder*, **2**, 285 (1951). A report on work started in 1938 and temporarily stopped in 1942. Freudenberg's proposed structures for lignin are reviewed. Lignin was assumed to be made of phenylpropane units as is also quebracho-catechin. In the latter, however, the phenolic hydroxyl groups are free whereas in lignin they are blocked by etherification and are inactive as regards tanning. The authors had planned 20 years earlier to open the ether linkages and so to form true tannins, but found what an important role molecular size plays in tanning action. Extensive demethylation of a sulfite waste liquor from spruce wood was possible with acid, especially with hydriodic acid, but a tanning material was not obtained because molecular size increased. Freudenberg had found that fusion of lignin with alkali at 270°C. or above decomposed it exothermally into protocatechuic acid and a resin. In 1938 the authors found that this resin was an outstanding tanning material resembling quebracho in tanning strength and character (French patent 878,121). Less drastic fusion conditions were desirable. Fusion at 150° removed sulfo and nearly all methyl groups. From the fusion product hydrochloric acid precipitated a resin that was soluble in the slightly acid region and, at pH 4-6, had a tanning action quite similar to that of quebracho or mimosa. Improved yields were also obtained by using only one part of alkali to one part of lignin material at a temperature of 240-280°C. Approximately 25 per cent of the product was soluble and contained 15-20 per cent of protocatechuic acid. Solubility of the difficultly soluble fraction was greatly influenced by the presence or absence of air during fusion. Air increased the acid character of the resin. The resin, although only slightly soluble, produced a full leather, quite similar to quebracho tanned leather. As a lower fusion temperature would aid commercial production, a study was made of fusion at 200°C. This removed sulfo groups, but reduced methoxy content only slightly. On acidification a water insoluble resin was obtained, which could be sulfited to form a water soluble material, having a tanning action resembling that of a good vegetable tanning material (French patent 878,123). A tanning material could also be produced by treating the alkaline solution from the fusion with air and a sulfite (French patent 875,625). In 1942-43, 1,000 kilograms of such a tannin was made under the name Gerbstoff MKF (French patent 878,451). After treatment with methyl sulfate, the methoxy content of both the lignin and its fusion products were approximately 30 per cent. That of quebracho was 32 per cent. The following hypothesis regarding the changes during fusion were derived: (1). It is probable that alkali fusion, in addition to splitting off sulfo groups, and regardless of degree of demethylation, causes some decrease in molecular size. (2). It is possible that a hydroaromatic group becomes aromatic and a hydroxyl group that is already present, becomes phenolic and therefore able to tan. (3). It is possible that the fusion product contains a new, hitherto unknown, tanning group. I.D.C.

PATENTS

Process for Hardening Gelatin and Photographic Gelatin Emulsions. U. S. Pat. 2,586,168. F. J. Kaszuba, Binghamton, N. Y., assignor to General Aniline and Film Corp., N. Y. Appl. July 11, 1947. (1) The method of producing a hardened gelatin layer in a photographic silver halide element having no after-hardening tendency which comprises uniformly mixing therewith, prior to coating upon a support, a dimethylol-diketopeperazine hardening agent characterized by the following general formula:



wherein R represents a member selected from the class consisting of hydrogen, and an alkyl group of not more than 4 carbon atoms and a phenyl group. (2) The method of producing a hardened gelatin layer in a photographic silver halide element having no after-hardening tendency which comprises uniformly mixing therewith, prior to coating upon a support, 2,4-dihydroxybenzaldehyde and a dimethylol-diketopiperizine hardening agent characterized by the following general formula:



wherein R represents a member selected from the class consisting of hydrogen, and an alkyl group of not more than 4 carbon atoms and a phenyl group.

Hide and Leather Working Machine. U. S. Pat. 2,586,879. R. J. Stehling, Milwaukee, Wis., assignor to Chas. H. Stehling Co., Milwaukee, Wis. Appl. May 29, 1950. In a machine having companion pressure rolls, one of which is movable to and from its operative position coacting with the other roll which is nominally stationary but has limited movement toward and from the operative position of the movable roll, the combination of: fluid pressure responsive means for moving the movable roll to and from its operative position; fluid pressure responsible means for pressing the nominally stationary roll towards its companion; a variable volume constant pressure pump supplying fluid under pressure to both said fluid pressure responsive means; manually operable control means for governing the operation of the first named fluid pressure responsive means; and control means automatically rendering said second named fluid pressure responsive means operative as the movable roll assumes its operative position.

Method of Drying Leather to Ultimate Clean Condition. U. S. Pat. 2,586,985. A. R. Olson, Wakefield, E. B. McMillan, Marblehead, and W. H. Davis, Beverly, Mass., assignors to United Shoe Machinery Corp. Appl. June 6, 1950. A method for drying leather which comprises providing a rigid drying board having a dried undercoating applied in the

form of a solution of chlorinated rubber and neoprene and a second dried coating of a water-sensitive polymeric amide, slicking out a wet leather work piece upon said second coating with an interposed coating in the form of a paste of methylcellulose, passing air in contact with said work piece to dry the same, and stripping the dried work piece from the board in clean condition.

Process and Apparatus for Treating Hides. U. S. Pat. 2,587,485. W. O. Kline, Waynesboro, Pa., assignor to Frick Co., Franklin, Pa. Appl. May 24, 1945. Apparatus for drying material at sub-freezing temperatures, drying by sublimation comprising subjecting material to be dried to flow of air having a dewpoint lower than the temperature of the material and a dry bulb temperature below freezing to cause absorption of moisture from the material by air.

Tanning Agent. Brit. Pat. 620 679. Progil, Apr. 23, 1946. Tanning agents are prepared by the sulfonation in vacuo of a phenol-formaldehyde type resin with an amount of acid less than that required for the complete sulfonation of the phenol in the resin, but sufficient to ensure that the resin is rendered completely soluble in water, the pH of the product being then brought to 3-4, e.g., by complete neutralization with ammonia or soda, followed by the addition of an organic acid. Urea may be added to the resin in its preparation. Sulfonation may be effected below 100°C. Examples relate to the preparation of phenol and cresol formaldehyde resins.

Tanning Agent. Brit. Pat. 620,839. Progil, Apr. 26, 1946. Tanning agents are prepared by treating a phenol-formaldehyde type resin in vacuo with a product obtained by sulfonation of naphthalene, phenol, cresol or xylenol. The resin is prepared in a slightly acid medium, and dehydrated in vacuo. A small amount of urea may be added to the resin in its preparation, or during treatment with the sulfonated product. The latter may be mixed with formaldehyde. The mixture of resin and sulfonated product is heated in vacuo at 80-90°C. for, say, 1-4 hours and the product neutralized to pH 3-4.

Degreasing Hides and Skins. Brit. Pat. 620,783. J. Burchell, J. H. Sharphouse and Imperial Chemical Industries. Dec. 11, 1946. Hides and skins are degreased by treatment with an aqueous liquor containing two or more surface active agents of the general formula $RZ(CH_2CH_2O)_xR'$, where R is an alkyl radical, saturated or unsaturated, containing not less than 10 carbon atoms, or a cycloalkyl, aralkyl or aryl radical, Z is—O—, —CO—, —NR″—or—CONR″—, where R″ is hydrogen or an alkyl radical, saturated or unsaturated, or a cycloalkyl or an aralkyl or an aryl radical or the group $(CH_2CH_2O)_yR'''$. Where R′ and R‴ are hydrogen or an alkyl radical the same or different, the surface active agents being selected from at least two of the three groups in which X if Y is absent or x + y is 1 to 5, 6 to 16, 17-30 respectively. Degreasing may be carried out on delimed, bated, drenched, pickled, depickled, partially or wholly tanned skins and in the presence of acid, alkali or salts. Mixtures of the condensation products of di-iso-butyl phenol with 8 mols. ethylene oxide and cetyl alcohol with 17 mols. ethylene oxide; octylcresol with 10 mols. ethylene oxide and cetyl alcohol with 30 mols. ethylene oxide; di-iso-butyl phenol with 8 mols. ethylene oxide and octyl cresol with 20 mols. ethylene oxide are specified in the examples.

Proofing Casein Threads and Fabrics. Brit. Pat. 621,753. Naamlooze Vennootschap Onderzoekingsimstituut Research. July 26, 1946. The tendency of casein threads or fabrics to swell in water is reduced and their acid-resistance increased by immersing the hardened threads for a short time in a hot solution of fimethylol derivative of a monosubstituted phenol or a monomethylol derivative of disubstituted phenol or a salt thereof, the methylol and other substituent groups occupying the ortho and para positions only on the phenol, after which they are dried and heated for some hours to a temperature above 100°C. The substituent group or groups of the phenol may be organic, e.g., methyl, or inorganic, e.g., chlorine. Examples are given in which formaldehyde hardened casein threads are immersed in aqueous 2:6-dimethylol paracresol at 70°C., removed, dried and heated for two hours at 130°C.

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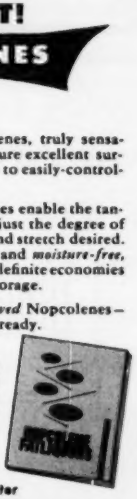

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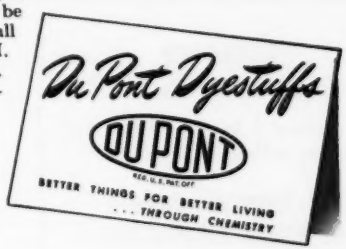

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